STUDIES OF ALPHA-RADIOACTIVITY IN THE MARINE ENVIRONMENT

by

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In terms of paragraph 8 of "Regulations for the Degree of Ph.D." I, as supervisor of the candidate L.V. Shannon, certify that I approve of the incorporation in this thesis of material that has already been published or submitted for publication. I further certify that this incorporated material is the work of the candidate himself unless specifically designated otherwise in the text.

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ABSTRACT

This dissertation deals with the alpha-radioactivity in the marine environment around South Africa, and the published literature relating to alpha-emitting nuclides in sea water and in marine organisms is surveyed in Chapter 1.

As a first step in the investigation, the total alpha-activity of some 400 samples of marine life was determined using the thick-source alpha-particle detection technique. The relative contributions of the thorium series nuclides and "excess" unsupported polonium-210 were determined by using the "thorium pairs" technique and by studying the variation of the total alpha count-rate with time. This is considered in Chapter 2.

The second phase of the investigation was to investigate the alpha-spectrum of marine life. This was done for several plankton samples using a large capacity ion-chamber. As expected several disequilibria were found to exist and the findings are discussed in Chapter 3. Unsupported polonium-210 accounted for the major proportion of the total alpha-activity in several marine groups, while radium-226 and daughters accounted for most of the long-lived radioactivity. Thorium series elements were also present. Using the ion-chamber data together with total alpha-counting data, an estimate of the radium-226 content of plankton was made.

After the ion-chamber experiments more detailed investigations, involving chemical extraction of polonium-210 and lead-210 and of thorium-232 and thorium-228, were made.

Chapter 4 deals with the polonium measurements in sea water and in marine organisms. A method is outlined for the determination of lead-210 and polonium-210 in sea water by solvent extraction, followed by electrodeposition and alpha-counting. Data are given for the lead-210 and polonium-210 content of twenty nine samples collected at a depth of 20 m in the sea around the Cape of Good Hope during March 1969. The mean activities of lead-210 and polonium-210 in these sea water samples were 38×10^{-15} c/l and 20×10^{-15} c/l respectively. Real variations in the concentrations of these nuclides were found to exist, and these could in part be ascribed to different water masses and current systems. The levels of unsupported polonium-210 in marine organisms were determined by repeated total alpha-counting. In addition to these measurements, the lead-210 and polonium-210 contents of 13 zooplankton and 4 phytoplankton samples collected during March 1969 were determined by chemical extraction, electrodeposition and alpha-counting. The mean values for lead-210 and polonium-210 in these zooplankton samples were 31 pc/Kg wet material and 380 pc/Kg wet material respectively. A correlation between these nuclides in zooplankton was found to exist, the lead-210 activity

being on the average one twelfth of the polonium-210 activity.

The contribution of the thorium series elements to the alpha-activity of marine life is dealt with in Chapter 5. A thorium extraction technique was used, and a disequilibrium between thorium-232 and thorium-228 was found to exist in plankton, the thorium-228/thorium-232 activity ratio being on the average about 15. The level of thorium-228 in marine organisms was typically about 20×10^{-18} g/g wet material.

Attempts were made to calculate the biogeochemical balance of several of the alpha-emitters in the marine environment. Using the data presented, and making certain stated assumptions, the removal times of these nuclides from the upper mixed layer were calculated. These times were found to be about 8 years for radium-226, thorium-228 and thorium-232, 5 years for lead-210 and 0.6 year for polonium-210.

Finally, the dependence of alpha-activity on species and oceanographic locality is discussed in Chapter 6. In the light of the results obtained it appears that polonium-210 and thorium-228 may prove valuable in tracing oceanographic processes occurring on a time scale of months to a few years. The main conclusions are summarized in Chapter 7.

This dissertation is presented in two volumes. All

the main results and discussion are included in the first volume. The second volume is in the form of an appendix and contains details of the equipment used, tables of data, sample calculations and a description of the oceanographic environment.

C O N T E N T S

VOLUME I

VOLUME II

1. ALPHA-RADIOACTIVITY IN THE SEA

The nuclear age dawned a quarter of a century ago with the explosion of the first atomic bomb in the Mexican desert. Since 1945 there have been rapid developments in the field of nuclear energy both for war and for peace, and associated with these developments has been the quest for knowledge about the radiation environment.

As fall-out products from nuclear weapon testing are predominantly short-lived beta- and gamma-emitters it was logical that considerable interest should be shown in the detection of this artificial fall-out. Consequently numerous investigations were undertaken to determine the artificially produced radioactivity in the atmosphere, on the land, in the oceans and in biological materials.

The natural radiation environment, in particular the natural alpha-radiation environment was somewhat neglected, and it is only during the last decade that interest in this field has gathered momentum. Modern techniques make possible the detection of a large number of nuclides at very low concentrations and the importance of establishing the natural radiation levels to which the biosphere is exposed is now widely recognised.

This dissertation deals mainly with the natural alpha-activity of sea water and of marine organisms found round South Africa, with the emphasis on the activity due to the natural fall-out product polonium-210 and to that due to

the thorium series elements. The purpose of the research was threefold. Firstly it was to establish the natural alpha-radioactivity background in, and the alpha-radiation dose received by marine life; secondly, to establish which nuclides produced this activity and to obtain some idea about their biogeochemical balance in the marine environment; thirdly, to investigate the possibility of using natural alpha-emitters as oceanographic tracers.

South Africa is in a unique oceanographic position. It is bounded by three oceans, the Atlantic on the West, the Indian on the East and the Southern to the South. All three have vastly differing physical, chemical and biological characteristics, and largely as a result of the interaction between these oceans, South Africa has a valuable fishery. The seas around South Africa are as yet relatively uncontaminated by artificial radioactivity because there has been no local effluent disposal from reactors. In view of the above the importance of establishing the levels of natural and artificial radioactivity in marine organisms becomes evident.

The remainder of this first chapter reviews the published data.

1.1 Alpha-Emitters in Sea Water

Most of the alpha-emitters found in the sea are members of the three naturally occurring radioactive series (viz. the thorium, uranium and actinium series). The geneological relationships in these three series are given by EVANS (1955), and the chief features of the uranium and thorium series are summarised in Table 2 in Section 2.1. Non series primordial alpha-emitters (e.g. samarium-147, neodymium-144 and cerium-142) have very long half-lives and/or a low isotopic abundance and therefore are omitted from the following discussion. Similarly, the very small contribution due to artificially produced alpha-emitters (e.g. FOLSOM, 1966) can usually be ignored. Some mention of these is nevertheless made in this review for completeness.

It is proposed to discuss the various alpha-emitters on an elemental rather than on a radioactive series basis.

1.1.1 Uranium

There are three naturally occurring isotopes of uranium present in the sea, namely, uranium-238, -234 and -235.

Among the earliest published data on the uranium content of sea water was that given by HERNEGGER and KARLIK (1935) as 1.1 µg/l. During the twenty years that followed various values ranging from 1 to 6 µg/l were

published, but most of these early results are on the low side in comparison with present day values. The low concentrations reported were probably due to inadequate storage procedures resulting in adsorption on the walls of the containers. KOCZY (1959) admitted that this possibily accounted for the low values obtained during the 1947-49 Swedish Albatros Expedition.

STEWART and BENTLEY (1954) obtained a mean reading of 2.49 µg/l for samples taken from the Pacific surf. Evidence in favour of these higher values was strengthened by RONA et al. (1956) who found an average of 3.3 µg/l for surface waters in the Atlantic and Pacific Oceans. Subsequently results given by MIYAKE and SUGIMURA (1964), SUGIMURA (1964), VISWANATHAN et al.(1965), MOORE and SACKETT (1964), MIYAKE et al. (1966) and others place the mean value for the oceans as 3±1 µg/l.

In a recent resume by SPENCE (1968) attention was drawn to the inconsistent results obtained by different techniques. He concludes that more determinations by rigorous analytical techniques are desirable to determine whether significant variations do in fact occur. Owing to the long residence time of uranium in the sea (GOLDBERG, 1963) it would be expected that it should be fairly evenly distributed.

The activity ratio of uranium-234/uranium-238 in the sea is about 1.14 (MOORE and SACKET, 1964; GOLDBERG and KOIDE, 1965; VEEH, 1968). This is rather surprising

as these isotopes are separated in the uranium series by nuclides with half-lives of less than a month. However, GOLDBERG and KOIDE (1965) attribute the fractionation of the two isotopes to a change in oxidation state from +4 to +6 as a direct result of the radioactive decay. An interesting feature was noted by BHAT et al. (1968) who reported marked disequilibria between uranium-238 and thorium-234 in surface waters, the activity ratio varying between 0.2 and 1.4. Thorium-234 was apparently removed from the surface and concentrated at a depth of about 100 m.

The contribution of the actinium series is typically 3% of that of the uranium series (alpha-activity wise). PICCIOTTO (1961) gives a value of 1.4×10^{-8} g/l for the uranium-235 content of sea water, corresponding to a uranium-235/uranium-238 activity ratio of 3% if the uranium content of the sea is taken as 3 µg/l. The contribution from artificially produced plutonium-239 is small as it is present in the ocean at very low concentrations (typically less than 0.003 pc/l-FOLSOM 1966).

1.1.2 Protoactinium

Protoactinium-231 is separated in the actinium series from uranium-235 by the beta-emitter thorium-231 which has a half life of about 25 hours. PICCIOTTO (1961) quotes

the concentration of protoactinium-231 in the sea as 5×10^{-14} g/l.

1.1.3 Thorium

In sea water there are four naturally occurring isotopes of thorium which are alpha-emitters, viz. thorium-232, -228, -230 and -227.

Thorium-230 exists in the sea at an apparent concentration of less than 10% of its equilibrium value with its uranium-234 parent, but the exact concentration appears to be uncertain. HOLLAND and KULP (1954) arrived at a value of 31×10^{-13} g/l while SACKETT *et al.* (1958) and PICCIOTTO (1961) gave the concentration as less than 3×10^{-13} and 6×10^{-13} g/l respectively. MIYAKE *et al.* (1964) gave a value an order of magnitude higher, while SUGIMURA (1964) quoted a range of values with upper and lower limits of $n \times 10^{-11}$ and $n \times 10^{-14}$ g/l respectively. More recently SOMAYAJULA and GOLDBERG (1966) measured the concentration of various thorium isotopes in Pacific waters, by towing sponges impregnated with ferric hydroxide at various depths. Their data indicate ionium concentrations in oceanic water varying between 1.2×10^{-14} and 3.7×10^{-14} g/l. Assuming that 2×10^{-14} g/l is a reasonable value for the thorium-230 concentration it is clear that there is a marked disequilibrium between this nuclide and its parent, the uranium-234/thorium-230

activity ratio being about a thousand.

KUZENTSOV (1969) considers that thorium-230 is present in a different form to thorium-232 in ocean water, in oceanic sediments and in suspensions. He assumes that most of the ionium present in the sea exists in hydrolytic forms which are sorbed onto suspension particles while thorium-232 is carried into oceans from the continents in the composition of residual minerals.

Early upper limits of thorium-232 and thorium-228 of the order of 10^{-8} and 10^{-18} g/l were given by SACKETT et al. (1958) and PICCIOTTO (1961). More recently MOORE and SACKETT (1964) obtained thorium concentrations in oceanic waters of the Atlantic at levels between 3.6 and 6.4×10^{-10} g/l, i.e. two orders of magnitude lower than original estimates. The findings of Moore and Sackett were subsequently confirmed by the work of SOMAYAJULA and GOLDBERG (1966) who obtained values between 2 and 6.5×10^{-10} g/l for the thorium-232 content of Pacific oceanic waters. The low concentrations of thorium in oceanic waters are thus in contrast to the much higher values (up to 2×10^{-7} g/l) reported in coastal waters and inland seas by several authors (e.g. LAZAREV et al., 1962; NIKOLAYEV et al., 1962; MIYAKE et al., 1964; SOMAYAJULA and GOLDBERG, 1966).

During 1969 further information about the thorium content of sea water was provided by three publications. In the first of these, MOORE (1969a) gave thorium-228

quoted values which implied an excess over thorium-228 of one or two orders of magnitude. In the Black Sea waters LAZAREV et al.(1965) found radium-228 at levels which give a radium-228/thorium-228 activity ratio of 500. Additional data on radium-228 and thorium-228 in the sea presented by MOORE (1969a) indicated that the radium-228/thorium-228 activity ratio varied between 0.3 and 3.0. The ratios indicate that thorium-228 is removed from surface water on a time scale of less than its half life (1.9 years). This removal was evident from an excess of thorium-228 at intermediate depths. In bottom water the activity ratio was close to or less than unity.

MOORE (1969a) considers that the excess of thorium-228 in ocean water is due to introduction of radium-228 from sediments in coastal regions. However SOMAYAJULA and GOLDBERG (1966), considered that diffusion of radium-228 from sediments was an unsatisfactory explanation of the excess of thorium-228 in the sea as thorium-228/thorium-232 ratios in the surface of oceanic sediments were near to equilibrium. They also considered that river input of excess radium-228 was unlikely due to the short half-lives of radium- and thorium-228, which would demand a radium-228 excess a few orders of magnitude higher than the activity of thorium-232. In an attempt to explain some features of the available data Somayajula and Goldberg hypothesised that thorium in sea water might be in the particulate phase. This would imply that

radium-228 could be preferentially leached from this phase, thereby giving rise to the observed excess of thorium-228 over thorium-232. They suggested that the activity ratios imply that at least 10 to 25 times the amount of thorium in solution is associated with the solid phase; if radium-228 is taken up by the solution with less than 100% efficiency, the amount of thorium in the solid phase must be correspondingly greater.

Support for the association of thorium-232 with solid phases was provided by DEMENT'YEV and SYROMYATNIKOV (1965) who studied the thorium isotopes in ground waters using centrifuging and dialysis techniques. They found that there was a tendency for thorium-232 to be associated with suspended matter and for thorium-228 to be in ionic solution. NIKOLAYEV et al. (1962) also favoured this association and attributed the large variations of thorium in the Sea of Azov to considerable amounts of suspended matter.

Thorium-227, the granddaughter of protoactinium-231, has a half-life of less than a month and is present in the sea at very low concentrations. PICCIOTTO (1961) gave its concentration as about 7×10^{-23} g/l, and for practical purposes it may be omitted from this general discussion.

1.1.4 Radium

There are two naturally occurring isotopes of radium

with long half-lives viz. radium-226 (1620 years) and the beta emitter radium-228 (6.7 years).

The concentration of radium in sea water was first accurately determined by EVANS et al. (1938) who found values ranging from zero to 3.3×10^{-13} g/l, the content increasing with depth. More recent determinations have confirmed this increase with depth (PETTERSSON, 1955; MIYAKE and SUGIMURA, 1964; BROECKER, et al. 1967).

MIYAKE and SUGIMURA (1964) found values of radium-226 ranging from $4\text{-}6 \times 10^{-14}$ g/l at the surface to $9\text{-}13 \times 10^{-14}$ g/l near the bottom in the Pacific Ocean. These observations were subsequently confirmed by BROECKER et al. (1967) and extended to the Atlantic Ocean. Broecker et al. found that radium-226 was fairly evenly distributed in the upper 500 m in both oceans, the mean concentration being about 4×10^{-14} g/l. Below 500 m, the radium-226 concentration increased with depth to about 8×10^{-14} g/l in the deep Atlantic water and about 16×10^{-14} g/l in corresponding deep Pacific water. They attributed the difference between the deep values in the two oceans to the different residence times of deep water in the Pacific and the Atlantic. SZABO (1967) reported a surface value of 4.5×10^{-14} g/l in the vicinity of the Bahamas.

Owing to the marked disequilibrium between radium-226 and its parent thorium-230, (radium-226 is present in the sea at levels of two orders of magnitude in excess

of the equilibrium value) it was generally accepted that radium is introduced into the ocean from sediments. Two mechanisms have been offered to account for this deficiency of radium in surface water relative to deep water. KOCZY (1958) suggested that this reflected radioactive decay during the period in which the surface water was isolated from the deep water. BROECKER et al. (1967) point out that this hypothesis would require much lower mixing rates than those calculated from the distribution of radiocarbon. CHOW and GOLDBERG (1960) suggested that the surface radium deficiency could have been brought about in a similar way to that for silicon and phosphorous. Radium in surface water is attached onto particulate matter that sinks, and the radium redissolves in the deep ocean. BROECKER et al. (1967) found no evidence for significant radium gradients in bottom water near the sediment interface. It has been suggested that radium may be associated with barium but TUREKIAN and JOHNSON (1966) found that in certain areas the relationship was doubtful. However a recent paper by WOLGEMUTH and BROECKER (1970) indicated a barium distribution similar to that of radium. Radium and barium do have similar chemical characteristics and in order to understand the radium distribution in the sea more fully it will be necessary for accurate radium-226/barium measurements to be made.

Like radium-226 in the uranium series, radium-228

in the thorium series is present in the sea at concentrations in excess of those predicted from radioactive equilibrium with its parent thorium-232. The work of MOORE (1969a,b) has provided useful information on the distribution of radium-228 in sea water. Absolute values quoted ranged from 0.9-100 dpm/1000 l in surface waters to 2-56 dpm/1000 l in deep waters. (These values correspond to the approximate range 2×10^{-18} - 2×10^{-16} g/l). MOORE (1969b), however, considers that the radium-228/radium-226 activity ratio is a more useful oceanographic parameter. Because of the 6.7 year half-life radium-228 could be a useful marine tracer for processes occurring in a 3-30 year time scale e.g. the measurement of eddy diffusion near the ocean floor and mixing rates across the main thermocline. Moore found large variations in the radium-228/radium-226 ratio in surface water with the highest values being recorded in coastal waters. Atlantic surface waters contained more radium-228 than Pacific surface waters. In concluding Moore considers that radium-228 is primarily supplied to the oceans by diffusion from thorium-232 bearing sediments.

Radium-224 has a 3.6 day half-life and should therefore be in equilibrium with its parent thorium-228.

1.1.5 Radon

Radon-220 and other following members of the thorium series have short half-lives and may be concluded to be in equilibrium with thorium-228.

Radon-222 in the uranium series however has a 3.8 day half-life and BROECKER et al. (1967) reported a radon-222/radium-226 activity ratio of about 0.5 in surface waters. They attributed this to diffusion of radon out of surface water into the atmosphere. Following radon-222 are several short-lived nuclides, which with the exception of lead-210 and daughters may be expected to be in equilibrium with radon.

1.1.6 Polonium and Radiolead

The radioactivity resulting from the beta emitter, lead-210 and its alpha-emitting daughter polonium-210 in the natural environment has been the subject of increasing attention in recent years. Radon-222 emanating from the surface of the land escapes into the atmosphere, where it decays via short lived daughters to lead-210 and its daughters. Several authors (BURTON and STEWART, 1960; BLIFFORD et al., 1952; PATERSON and LOCKHART, 1964; LAMBERT et al., 1966; PIERSON et al., 1966; TER HAAR et al. , 1967) have given data for lead-210 and polonium-210 in the atmosphere and rains. The lead-210 activity

of the lower troposphere is about 1×10^{-2} dpm/kg while the ratio of the activities of polonium-210 to lead-210 in ground level air is typically about 0.14 (BURTON and STEWART, 1960; PIERSON et al., 1966). Data on these nuclides in rain over land are numerous for localities in the northern hemisphere (BURTON and STEWART, 1960; BLIFFORD et al., 1952; PIERSON et al., 1966; TER HAAR et al., 1967) but few results are available for the southern hemisphere (BLIFFORD et al., 1952; PIERSON et al., 1966). From these publications a typical value for lead-210 in rains over the northern hemisphere lies in the range 1 to 5 pc/l and somewhat lower (about 0.5 to 2 pc/l) in the southern hemisphere. The polonium-210 to lead-210 ratio in rain water is about 0.1 - 0.3; i.e. approximately similar to that observed for the troposphere (BURTON and STEWART, 1960; LAMBERT and NEZAMI, 1965). Calculations of the residence time of lead-210 in the atmosphere based on measurements of the polonium-210/lead-210 ratio have been made (BURTON and STEWART, 1960; PIERSON et al., 1966; LAMBERT and NEZAMI, 1965) and provide values ranging from 20 to 40 days.

Very little work appears to have been done on either polonium-210 or lead-210 in sea water. Lead-210 levels were first reported in 1961 by RAMA et al.(1961) and subsequently considered in more detail by GOLDBERG (1963). These observations were made on large sea water samples collected in the Eastern Pacific. The method employed by

RAMA et al. (1961) involved coprecipitation of the lead followed by anion exchange and beta-counting. The lead-210 content ranged from about 0.10 dpm/l (6×10^{-16} g/l) in the upper water layers to 0.28 dpm/l (16×10^{-16} g/l) at a depth of 2000 m. From these results, after making various assumptions, a biological removal time for lead-210 of 2 years was calculated by the authors.

POPOV (1964) quoted the polonium-210 content of sea water as 2×10^{-17} g/l, but up to the time of writing as far as can be ascertained, no other values for the polonium-210 level in sea water had appeared in scientific journals apart from those of SHANNON et al. (1970), although two institutional reports (FOLSOM, 1966; BATTELLE-NORTHWEST REPORT, 1968) provide some data. The method of Folsom used a scavenger (ferric hydroxide) in fifty-litre sea water samples followed by alpha-analysis. A mean value of 0.037 pc/l (i.e. 0.08 dpm/l or 8×10^{-18} g/l) was reported for samples collected from Scripps Pier. A recent paper by KAURANEN and MIETTINEN (1970) indicated variable values for polonium-210 and lead-210 in brackish waters of the Gulf of Finland. Details of the work of SHANNON et al. (1970) are embodied in this dissertation.

A summary of the concentrations of the main uranium, thorium and actinium series nuclides in the sea is given in the following table.

TABLE 1 : Concentrations of the main uranium, thorium and actinium series elements in sea water.

Uranium Series	g/l	c/l
Uranium-238	$2\text{-}4\times10^{-6}$	$6\text{-}12\times10^{-13}$
Uranium-234	$1\text{-}2\times10^{-10}$	$6\text{-}12\times10^{-13}$
Thorium-230	$1\text{-}4\times10^{-14}$	$2\text{-}8\times10^{-16}$
Radium-226	$4\text{-}16\times10^{-14}$	$4\text{-}16\times10^{-14}$
Lead-210	$6\text{-}16\times10^{-16}$	$5\text{-}12\times10^{-14}$
Polonium-210	$4\text{-}8\times10^{-18}$	$2\text{-}4\times10^{-14}$
Thorium Series		
Thorium-232	$2\text{-}6\times10^{-10}$	$2\text{-}6\times10^{-17}$
Radium-228	$2\times10^{-18}\text{-}2\times10^{-16}$	$4\times10^{-16}\text{-}4\times10^{-14}$
Thorium-228	$10^{-19}\text{-}10^{-16}$	$8\times10^{-17}\text{-}8\times10^{-14}$
Actinium Series		
Uranium-235	1.4×10^{-8}	3×10^{-14}
Protoactinium-231	5×10^{-14}	3×10^{-15}
Thorium-227	7×10^{-23}	2×10^{-14}

1.2 Alpha-Activity of Marine Organisms

Very little data has been published on the above topic. An article by MARSDEN (1963) indicated high alpha-activities and interesting problems associated with possible disequilibria in the radioactive series. CHERRY (1964) measured the gross alpha-activity of marine plankton by the total alpha-counting method of TURNER et al. (1958a) and found that the alpha-activity of zooplankton varied between 1.8 and 12.0 pc/g dry material, while phytoplankton values ranged from 3.8 to 95 pc/g. The thorium series contribution was typically about 25% while results indicated the presence of excess polonium-210. The findings of Cherry were subsequently confirmed by SHANNON (1969) who reported a mean alpha-activity of 5-6 pc/g dry material for both zooplankton and phytoplankton. Of this, unsupported polonium-210 accounted for about 4 pc/g in zooplankton and about 2 pc/g in phytoplankton.

Data on the concentrations of uranium and thorium series elements and also plutonium-239 in various marine organisms are given below in the following discussion.

1.2.1 Uranium

KOCZY and TITZE (1958) analysed the shells of two species of marine molluscs for uranium and detected this element at concentrations ranging from 0.5 to 2.1 ppm

in seven samples. These results were typically an order of magnitude higher than those obtained by TATSUMOTO GOLDBERG (1959) who gave values between 0.004 and 0.21 ppm for a range of calcareous organisms. In corals the uranium content is typically 2.5 - 5.5 ppm (BARNES et al., 1956; TATSUMOTO and GOLDBERG, 1959)

A number of uranium analyses were carried out on fish flesh by ATEN et al.(1961). These authors concluded that the average uranium content was 2×10^{-3} g/kg wet (fresh) weight.

Although uranium has been measured in plankton in inland seas and lakes (notably in U.S.S.R.), little is known about uranium in marine plankton. The role of living organisms in the uranium "migration" in Lake Issyk-Kul in Russia was investigated by KOVALSKI (1965). He concluded that the chief concentrator was an algae of the Charophytes family and attributed the enrichment of uranium in silts to accumulation of uranium by this organism during its lifetime. He found that the uranium content decreased along the food chain.

1.2.2 Plutonium

Plutonium-239 (2.4×10^4 year half-life) has been detected in various marine organisms but at very low concentrations - e.g. FOLSOM (1966) gave its level in Mytilus as about 0.6 pc/kg wet (fresh) material.

1.2.3 Thorium

Until recently no measurements on thorium isotopes in marine organisms had been made. CHERRY (1964) indicated that the alpha-activity due to thorium series elements in marine plankton collected off South Africa was of the order of 1 pc/g dry material, while SHANNON (1969) reporting on research carried out in 1965 and 1966 found that the thorium series activity was very variable in both zooplankton and phytoplankton, typical values ranging from 0.2 pc/g to 2.0 pc/g dry material. Shannon attributed the variations to coastal upwelling along the west coast of South Africa and possible cyclic oceanographic processes taking place in the vicinity of the Subtropical Convergence. Evidence as to the state of equilibrium in the thorium series was conflicting.

MOORE and SACKETT (1964) and MOORE (1969a,b) made use of thorium-228 measurements on recent shells to predict radium-228 concentrations in coastal waters. Disequilibria of thorium isotopes in recent and fossil marine molluscan shells were investigated by BLANCHARD et al. (1967). The work was undertaken in an attempt to determine the age of marine fossils. The predominant thorium alpha-activity in shells of living molluscs was associated with thorium-228,presumably as a result of the decay of radium-228. Thorium-230 concentrations in modern marine shells were close to zero viz. probably less than 1% of the equilibrium quantity.

Preliminary results on the thorium content of South African marine plankton were given by CHERRY et al.(1969). Thorium-228 was present in zooplankton at levels ranging from 2×10^{-18} (Subantarctic Water) to 27×10^{-18} (Walvis Ridge Water) g thorium-228/g wet plankton. Corresponding values for phytoplankton varied between 9×10^{-18} (Subantarctic Water) and 65×10^{-18} (Agulhas Current) g thorium-228/g wet plankton. The results indicated the possible use of thorium-228 as natural oceanographic tracer. The plankton data embodied in CHERRY et al.(1969) and additional data are considered in detail in Chapter 5 of this dissertation.

1.2.4 Radium

Radium was detected in zooplankton as early as 1932. BRUNOVSKI (1932) reported radium at a level of 2×10^{-13} g/g ash in Calanus finmarchicus. EVANS et al.(1938) quoted a content of 4×10^{-14} g radium/g dry zooplankton from the Pacific Ocean. More recently SZABO (1967) reported a mean radium content of 8.4×10^{-14} g radium/g dry zooplankton from the Providence Channel area in the Bahamas. It appears therefore that radium-226 is present in zooplankton at levels of about $n \times 10^{-14}$ g/g dry material.

One of the first radium measurements on phytoplankton (diatoms) was made by FÖYN et al.(1939) who obtained a

value of 2×10^{-12} g radium/g dry phytoplankton. KOCZY and TITZE (1958) gave the radium content of plankton from the North Sea as 2.75×10^{-12} g radium/g dry material. They did not state whether this was phytoplankton or zooplankton, but judging from details of its chemical composition it was almost certainly phytoplankton. These values are in good agreement with that of CERRAI et al. (1964) who indicated 1.9×10^{-12} g radium-226/g mixed plankton from the Tyrrenian Sea.

Results summarised by VINOGRADOV (1953) indicated that the average concentration of radium in marine algae was about 1×10^{-14} g radium-226/g wet material. This value corresponds to approximately 5×10^{-14} g radium-226/g dry algae, a figure in close agreement with those given by WIESNER (1938), who found values ranging from 0.7 to 14×10^{-14} g radium/g dry material for samples from the Adriatic and 7.5×10^{-14} g radium/g dry material for algae from the North Sea. Data on radium-226 in plankton collected around South Africa will be reported in this dissertation.

SZABO (1967) quotes measurements of radium in fish by other workers as between 0.4 and 2.7×10^{-13} g radium/g ash. HOLTZMAN (1969) reported the mean radium content of nine samples of ocean fish as 1.6 pc radium-226/kg wet soft tissue and 53 pc/kg ash in hard tissue (bone). These activities correspond to concentrations of 1.6×10^{-12} g radium-226/kg wet soft tissue and and 53×10^{-12}g

LITTLE and McGANDY, 1966; HOLTZMAN, 1966; KAURANEN and MIETTINEN,1969). More recently data have been provided for the concentration of these nuclides in marine life.

CHERRY (1964) indicated that the decrease in total alpha-activity of dried plankton over a time scale of three months was possibly due to the presence of unsupported polonium-210, and subsequently SHANNON and CHERRY (1967) reported excess polonium-210 at levels of about 4.7 pc/g dry weight for zooplankton and 2.8 pc/g dry weight for phytoplankton.†

HOLTZMAN (1969) analysed a number of samples of fish, molluscs and marine mammals for polonium-210 and lead-210 by wet ashing followed by electroplating and alpha-counting (lead-210 was determined by replating after four months and measuring the polonium-210 that had grown into the plating solution). Results indicated mean polonium-210 and lead-210 contents of ocean fish flesh of 3 and 1.7 pc/kg wet material respectively. The bones of pelagic fish had a specific activity for both polonium-210 and lead-210 of about 30 pc/100 g ash, a value about $\frac{1}{3}$ that in bovine and about twice that in human bone. In molluscs the concentration of these nuclides was one or two orders of magnitude

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†Data given by SHANNON and CHERRY(1967) and SHANNON (1969) are not embodied in this dissertation.

higher than in fish flesh. Lead-210 in seals averaged at about 3 pc/kg wet material. The highest activity recorded for both polonium-210 and lead-210 was in a single copepod (Calanus plumchrus) sample, the respective concentrations being 1137 and 121 pc/kg wet material respectively, indicating a polonium-210/lead-210 activity ratio of 9.4. The corresponding ratio in Euphausia pacifica was 7.1, in squid 14.4, and in the kidney of a whale 44.2. From these results it is evident that polonium-210 is in excess of its parent in many samples of marine life.

BEASLEY (1968) gave details of the polonium-210 and lead-210 content of various marine organisms. Typical values for concentration of these respective nuclides were 900 and 130 pc/kg wet material, the mean polonium-210/lead-210 activity ratio being about 10 i.e. in good agreement with the findings of HOLTZMAN (1969). The main features of Beasley's data were subsequently published by BEASLEY et al. (1969). In their discussion of levels of various radionuclides in fish and other organisms, these authors concluded that if marine protein concentrates are used as human food, the lead-210/polonium-210 pair may become the principal source of skeletal radiation dose.

2. TOTAL ALPHA-COUNTING OF MARINE ORGANISMS

2.1 Background and Theoretical

Most of the alpha-emitting nuclides found in nature are members of the three naturally occurring radioactive series, namely, the uranium series, the thorium series and the actinium series. The contribution from the non-series primordial alpha-emitters (for example samarium-147, neodymium-144 and cerium-142) is small. Samarium-147 and cerium-142 do not exceed 15% in isotopic abundance, while neodymium-144 has a very long half-life. Artificially produced plutonium-239 is present in the sea at very low levels and may for practical purposes be neglected. The contribution of the actinium series in nature is typically about 3% that of the uranium series. EVANS (1955) gives the genealogical relationships in the three naturally occurring series. The chief feature of the uranium and thorium series are considered in Table 2.

TABLE 2 Summary of the characteristic of the uranium and thorium series

Uranium (4n+2) Series	Thorium (4n) Series
8 alpha-emitters	6 alpha-emitters
Uranium-238 is head member of series ($T_{\frac{1}{2}}$=4.5 × 10^9 years)	Thorium-232 is head member of series ($T_{\frac{1}{2}}$=1.4 × 10^{10} years)
Four other long-lived nuclides, namely,	Two other long-lived nuclides, namely,
Uranium-234 ($T_{\frac{1}{2}}$=2.5 × 10^5 years)	Radium-228 ($T_{\frac{1}{2}}$=6.7 years)
Thorium-230 ($T_{\frac{1}{2}}$=8 × 10^4 years)	Thorium-228 ($T_{\frac{1}{2}}$=1.9 years)
Radium-226 ($T_{\frac{1}{2}}$=1620 years)	
Lead-210 ($T_{\frac{1}{2}}$=22 years)	
Polonium-210 is longest lived ($T_{\frac{1}{2}}$=138 days) of remaining nuclides	Radium-224 ($T_{\frac{1}{2}}$=3.6 days) is longest lived of remaining nuclides
The alpha-energies increase approx. down the chain	The alpha-energies increase approx. down the chain.

2.1.1 Radioactive Equilibrium

Consider a series composed of a radioactive nucleus A decaying to a radioactive nucleus B which in turn decays to a radioactive nucleus C, with decay constants λ_A , λ_B and λ_C respectively. Provided the only supply of A is from a

source containing A_o nuclei at time t = 0, and provided the half-life of A is much greater than the half-life of B and C, then, if t is large compared with λ_B^{-1} and λ_C^{-1} it can be shown that to a very good approximation, $A\lambda_A = B\lambda_B = C\lambda_C =$ ..... When this is the case, then the series is in secular equilibrium.

The activity of a daughter member of the series rises with its own time constant to the activity of the parent. Several disequilibria exist in the three natural radioactive series in the marine environment, and these are discussed later.

2.1.2 Alpha-Ranges

Alpha particles, being the nuclei of helium atoms, and having energies in the range 4 MeV to 9 MeV, are a heavily ionizing form of nuclear radiation. (The relative biological effectiveness (R.B.E.) of alpha-radiation is usually quoted as 10 - e.g. FEDOROV, 1965).

Semi-empirical formulae show that the range of an alpha-particle in a medium is proportional to the alpha-range in standard air, and is a function of density, atomic weight and/or atomic number of the material. The semi-empirical formula used by TURNER et al. (1958a) was based on a suggestion of GLASSON (1922). However, whereas Glasson explicitly stated that the stopping power was proportional to $Z^{2/3}$ (Z is the atomic number of the material),

Turner et al. incorrectly assumed that the alpha-range was proportional to $Z^{2/3}$. In this dissertation the calculations follow the Glasson suggestion but take account of this error; full details are given in the Appendix (Section 10.3.1).

2.1.3 Thick Source Alpha-Counting

The theory of both thick and thin source alpha counting is straightforward. It was originally developed by FINNEY and EVANS (1935) and applied to early ion chamber alpha-counting. More recently TURNER et al. (1958a) applied it to the scintillation counting of human tissues.

The basic theory of thick source counting assumes that the alpha-emitters are homogeneously distributed in the medium and that all alpha-rays down to zero energy are detected. In order that the former condition be satisfied the sample must be ground down to micron size or smaller and thoroughly mixed. A homogeneous sample is essential if good qualitative accuracy is required as inhomogeneities (for example "hot spots") can introduce a significant error in the results obtained. If alpha-particles down to zero are detected with 100% efficiency, and if other contributions (e.g. beta- and gamma-rays) are detected with 0% efficiency, then the number of "counts" observed per unit time will correspond to the number of alpha-particles N_o emerging from an area A per unit time. Provided that the

area of the source is much greater than the square of the dimensions of the alpha-range, and also that the thickness of the source is greater than the range, we may write:

$$N_o = \frac{NRA}{4}$$

where N is the number of alphas emitted per unit volume per unit time (hour) in the sample and R is the alpha-range in the sample. Furthermore the strength of the active material in curies per gram is given by

$$S = \frac{N_o}{RA\rho} \quad 3.008 \times 10^{-14} \text{ c/g}$$

From the above it is immediately evident that the activity of a particular sample may be obtained by multiplying the corrected "count rate" N_o by a predetermined multiplying factor. The result is independent of the density - that is the degree of packing of the sample. This fact was confirmed experimentally by TURNER et al. (1958). A rule of thumb formula that is useful in thick source alpha-counting is,

$$\text{Activity in pc/g} = \frac{5N_o}{\text{Source area in cm}^2}$$

where N_o is in counts/hr.

2.1.4 Alpha-Pairs Technique

The alpha-pairs technique has been successfully used by TURNER et al.(1958a) and others to assess the relative contributions made by the three natural radioactive series whilst performing total thick source counting. Use is made of a paralysis circuit to isolate from its predecessor the rapid transition from polonium-216 ($T_{\frac{1}{2}}$ = 0.158 sec) to lead-212 in the thorium series and from polonium-215 ($T_{\frac{1}{2}}$ = 0.0018 sec) to lead-211 in the actinium series.

Assuming there is no correlation between the directions of successive alpha-emissions, the total thick source theory can be extended (CHERRY, 1963) to give,

$$P = \frac{nAR_1}{8} \left(1 - \frac{R_1}{3R_2}\right)$$

where P is the number of genuine alpha-pairs emerging from an area A per unit time,

n is the number of disintegrations per unit volume per unit time of the nuclide responsible for the emission of the first alpha-particle in the "pair",

R_1 and R_2 are the alpha-ranges in the sample of the two successive alpha-particles in the "pair".

Suppose we have a sample containing the uranium and thorium series elements and none of those of the actinium series. The total of alpha-counts from the sample will include "thorium" pairs due to the nuclides radon-220 and

polonium-216 with a mean spacing of about 0.2 seconds. If radioactive equilibrium can be assumed, then the number of pairs will be proportional to the concentration of the head members of the thorium series. If thorium-228 is the effective head member, then the pairs rate in pairs per hour is given by,

$$P = 1.4 \times 10^{16} A \text{ (thorium-228) } R_1 \rho \left(1 - \frac{R_1}{3R_2}\right)$$

where ρ is the density of the material and (thorium-228) is the concentration of this nuclide on a weight for weight basis.

The pairs technique is usually only applied to the counting of materials with a low activity. Results are corrected for the contribution of random pairs - see Section 10.3.2 for sample calculation.

2.2 Experimental

2.2.1 Collection of Samples

Plankton samples were collected in the oceans around South Africa between 1967 and 1969 for alpha-analysis. The positions of the oceanographic stations occupied are to be found in the Appendix (Chapter 10).

Although the sea around South Africa is relatively rich in marine plankton, the collection of sufficient material for the preparation of a suitable source for

counting is often a time-consuming process. Usually several hauls of the nets are necessary to procure an adequate sample, so that special cruises had to be arranged in order to obtain bulk plankton samples from a wide area. Various standard oceanographic nets were used to obtain the samples.

Plankton samples for total-counting were either processed immediately on the ship or if this was not possible they were preserved with minimum quantities of formaldehyde solution. Sufficient portions of the samples were kept for biological analysis and the remainder processed for counting. Formaldehyde was found to be suitable as a preservative, as, firstly, it has a low alpha-activity and secondly, most of the formaldehyde is removed by washing during the processing of the plankton. When a formaldehyde solution is heated to dryness, a white crystalline solid, m.p. 121-123°C is obtained. This is known as paraformaldehyde $(CH_2O)_n.H_2O$, and it appears to be a mixture of polymers, n having values between six and 50 (FINAR, 1959). Paraformaldehyde reverts to formaldehyde when heated. In order to check any possible contamination from formaldehyde, paraformaldehyde was prepared from a 38% formaldehyde solution and counted in the usual way. The activity of paraformaldehyde was found to be less than 1 pc/g. As only small traces of this compound will be found in the plankton after processing, its contribution towards the activity of the

plankton is negligible.

Samples of fish and other forms of relatively large marine species were either processed immediately or deep-frozen until such time as they could be analysed.

The method of total-counting is similar to that used by TURNER et al. (1958a) , CHERRY (1963) and others. Details are as follows:

2.2.2 Sample Preparation

The plankton samples were filtered through meshes of varying sizes (a) to separate different species and (b) to remove excess moisture from the plankton. Size groups were separated whenever possible. For example, a sample containing a mixture of zooplankton and phytoplankton or euphausiids and copepods could be sorted simply by filtering the sample through a suitably sized system of mesh filters. After separation, the sample was washed well with distilled water, and allowed to drain until it ceased to drip. After the excess moisture had been allowed to drain off, the plankton was transferred to a porcelain evaporating dish, and subsequently dried for four hours in a thermostatically controlled oven at 105°C. This drying procedure was applied throughout.

Some of the plankton samples were split to check for possible losses of alpha-radioactivity during drying, one part being dried by oven as above, and the other part being

freeze dried. The freeze drying technique was similar to that used by HASSON and CHERRY (1966) for the lyophilization of blood, and involved freezing the plankton in a glass flask by rotating it in a mixture of dry ice and alcohol. The flask was then evacuated by means of a high capacity pump via an intermediate adaptor unit, the latter being cooled by a dry ice-alcohol mixture. Samples were dried for 24 hours by this method.

Wet weights and dry weights were recorded for all the samples in order to make an estimate of the activity of the plankton in its natural state in the sea. The difficulty with such evaluations is that it is virtually impossible to estimate the wet weight accurately. By merely allowing the plankton to "drip-dry" through a suitable filter, some water must necessarily be trapped on the surface of, and between the individual planktonic organisms, and this will result in a high wet/dry concentration factor. The application of pressure or vacuum to remove interstitial moisture tends to dehydrate the actual organisms, with the consequent loss of body fluid. In view of this, the latter procedure was avoided, and the wet weights obtained by "drip-drying". In order to eliminate any possible error introduced in the results, all activities in the tables are expressed both on a dry and on a wet basis.

In the case of fish and other large organisms it is possible to estimate the wet weight with a good degree of

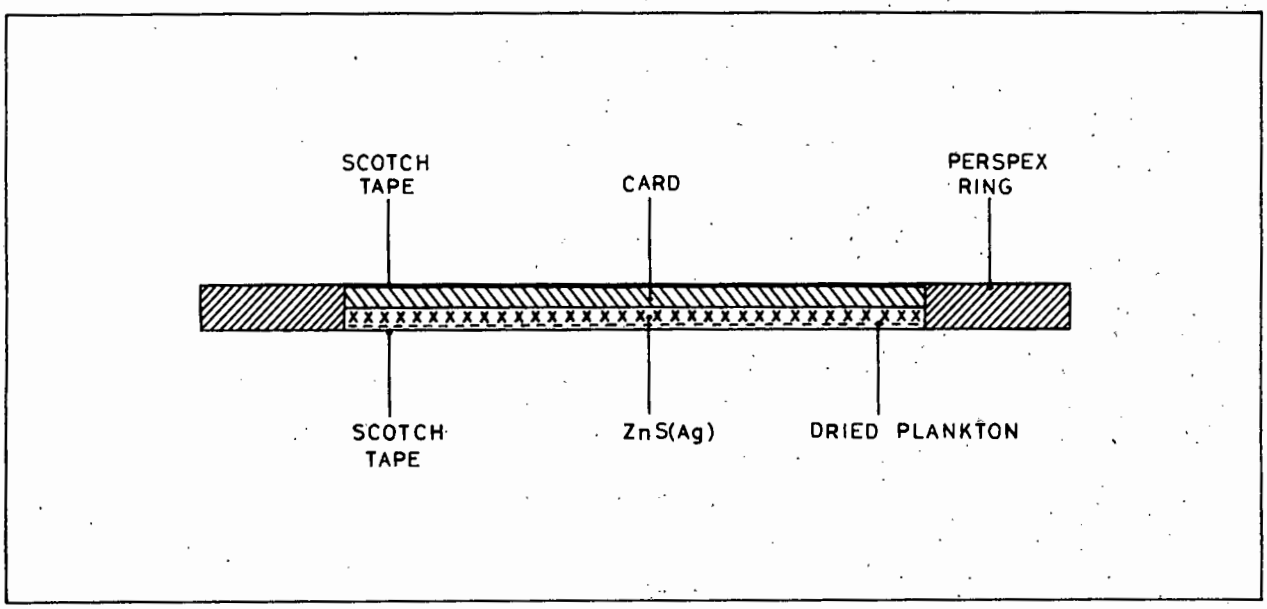

FIG. I CONSTRUCTION OF DISC

accuracy. Such samples were passed through a liquidiser prior to drying so as to ensure homogeneity of the sample.

After drying, the samples were transferred to a high speed coffee mill and homogenised for a few minutes. They were subsequently finely ground by means of a mortar and pestle.

The construction of the source (disc) for total counting is shown in Fig. 1. Cellulose adhesive tape was stretched over a perspex ring, and trimmed. Silver activated zinc sulphide powder was sprinkled over the sticky surface of the tape and the disc agitated until no more powder would adhere to the tape. This formed the phosphor. Levy-West G231 ZnS (Ag) was used throughout and was found completely satisfactory. (The range of the grain size for G231 is 20-40 microns).

After construction of the phosphor, the ground material to be counted was packed thereon, making sure that the whole surface received an adequate covering (at least 1 mm which is more than ten times larger than the largest alpha-particle range involved). A cardboard disc was then fitted on top of the plankton and the disc finally sealed with cellulose tape. The completed sources (discs) were stored for three weeks to settle before counting, thus avoiding emanation problems.

In general, perspex rings having an internal diameter of 7.6 cm were used for the construction of the discs, but sometimes the paucity of available sample material

necessitated the use of rings with an internal diameter of 3.8 cm.

The chief advantages of the above method of sample preparation are (a) the disc is a sealed unit and emanation problems involving the gases thoron and radon are accordingly reduced (b) contamination problems are minimal and (c) very low backgrounds (typically about ½ a count per hour for a 7.6 cm disc) are recorded, while at the same time alpha-particle detection efficiencies of close to 100% are realised. The sensitivity of detection of the technique is about 0.03 pc/g dry material.

2.2.3 Corrections Applied

Various corrections must be applied, both to the count-rate and the pairs-rate. The total count-rate must be corrected for background. The background is due to (a) photomultiplier tube noise - typically about half a count an hour, and (b) blank phosphor count-rate which is of the order of half a count an hour. The total background must be subtracted from the sample count-rate. A correction factor must also be applied to the total count-rate if the counter is operated off the alpha-plateau (see Section 10.2.1).

The pairs-rate must be corrected for (a) background pairs from spurious electronic causes - usually negligible (less than 0.01 pairs/hr) - (b) spurious pairs due to

random coincidence of alpha-particles, and (c) the finite dead-time of the electro-mechanical register.

The spurious pairs-rate is given by the following formula, which is an extension of that derived by CHERRY (1963)

$$S = N^2T$$

where N is the observed total count-rate and T is the dead-time of the electro-mechanical register. S must be subtracted from the total pairs count.

Radioactive decay is a probability process, and statistically, owing to the finite dead-time of the register circuit, all the pairs are not recorded. A correction factor f is applied after correcting for the background and spurious pairs-rate, and can be shown to be

$$f = \frac{1}{1 - \exp\left(\frac{-0.693T}{T_{\frac{1}{2}}}\right)}$$

where T is the dead-time of the register, and $T_{\frac{1}{2}}$ is the half-life of polonium-216 (0.158 second) - see Section 10.3.2.

2.3 Results and Discussion

2.3.1 General

The total alpha-activities have been corrected for unsupported polonium-210 decay as described in Section 10.3 and all individual sample results given in Table 19 in the

Appendix are as at time of collection. Unless otherwise stated, all activity values given in this dissertation are applicable to the dates on which the samples in question were collected.

The mean gross alpha-activities of various groups of marine organisms are summarised in the following Table 3.

TABLE 3 Mean alpha-activities of various marine organisms at time of collection (errors are standard errors of the mean)

Organism	No. of Samples	Gross Alpha-Activity		Internal Alpha Radiation Dose
		pc/g(dry)	pc/Kg(wet)	millirem/yr
Zooplankton	211	11.3±0.6	850±45	800
Agulhas Phytoplankton	10	47.4±8.5	2200±400	500
Other Phytoplankton	24	11.4±0.2	630±90	150
Pelagic fish (whole)	13	4.9±0.9	1300±250	1200
Demersal fish (whole)	18	1.3±0.2	380±55	350
Demersal fish (flesh)	7	0.7±0.2	200±50	190
Demeral fish (liver)	4	3.9±1.1	1000±290	900
Mollusc soft tissue	15	5.5±1.2	1600±360	1500
Mollusc shell	15	0.8±0.3	700±260	650
Rock Lobster tail flesh	9	0.6±0.1	150±30	140
Rock Lobster shell	9	0.9±0.2	430±70	400
Rock Lobster digestive gland	9	36.6±7.3	14800±2900	14 000
Seaweed	13	1.8±0.2	300±30	280

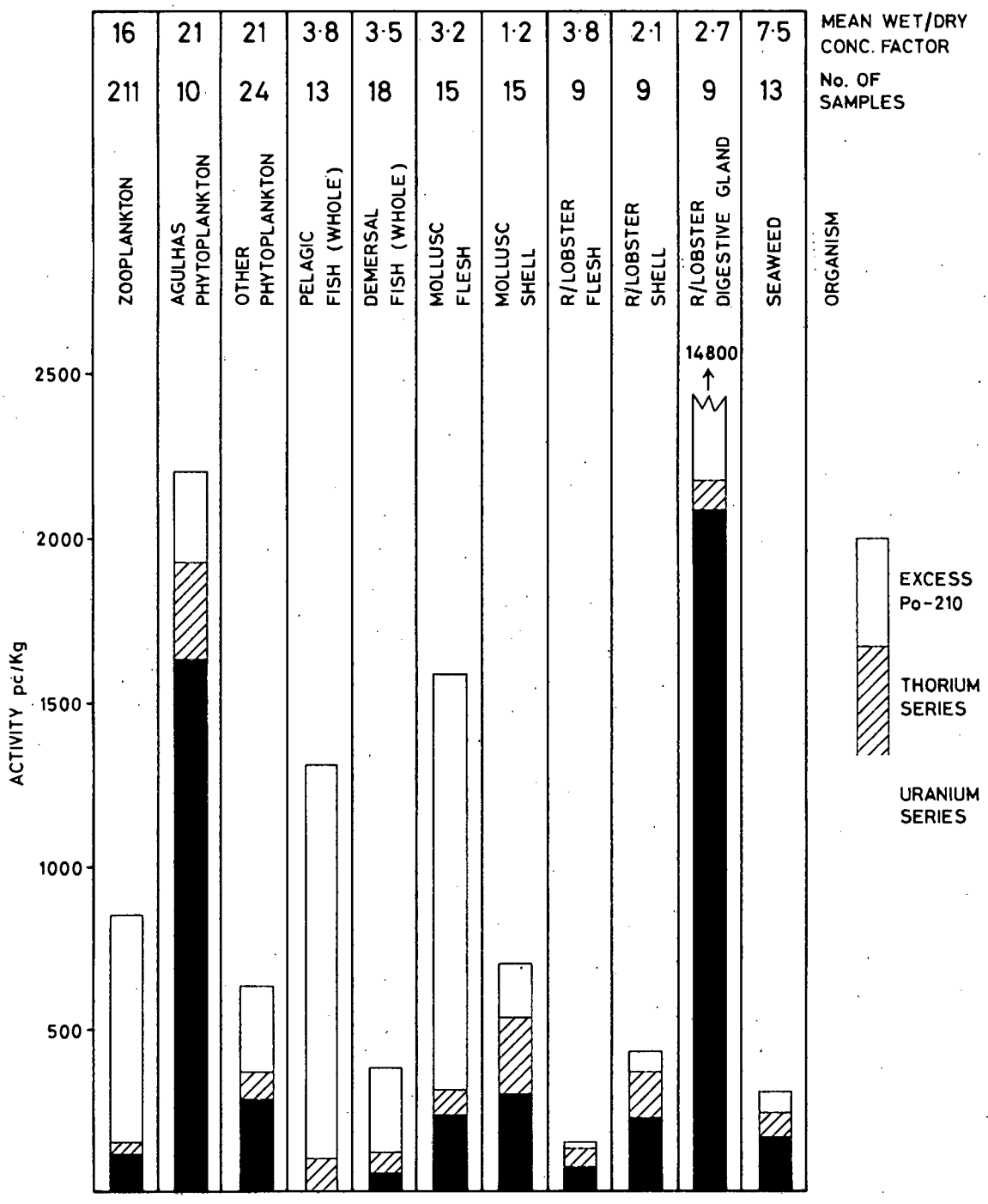

FIG. 2 ALPHA-ACTIVITY IN VARIOUS MARINE ORGANISMS (pc/Kg wet material)

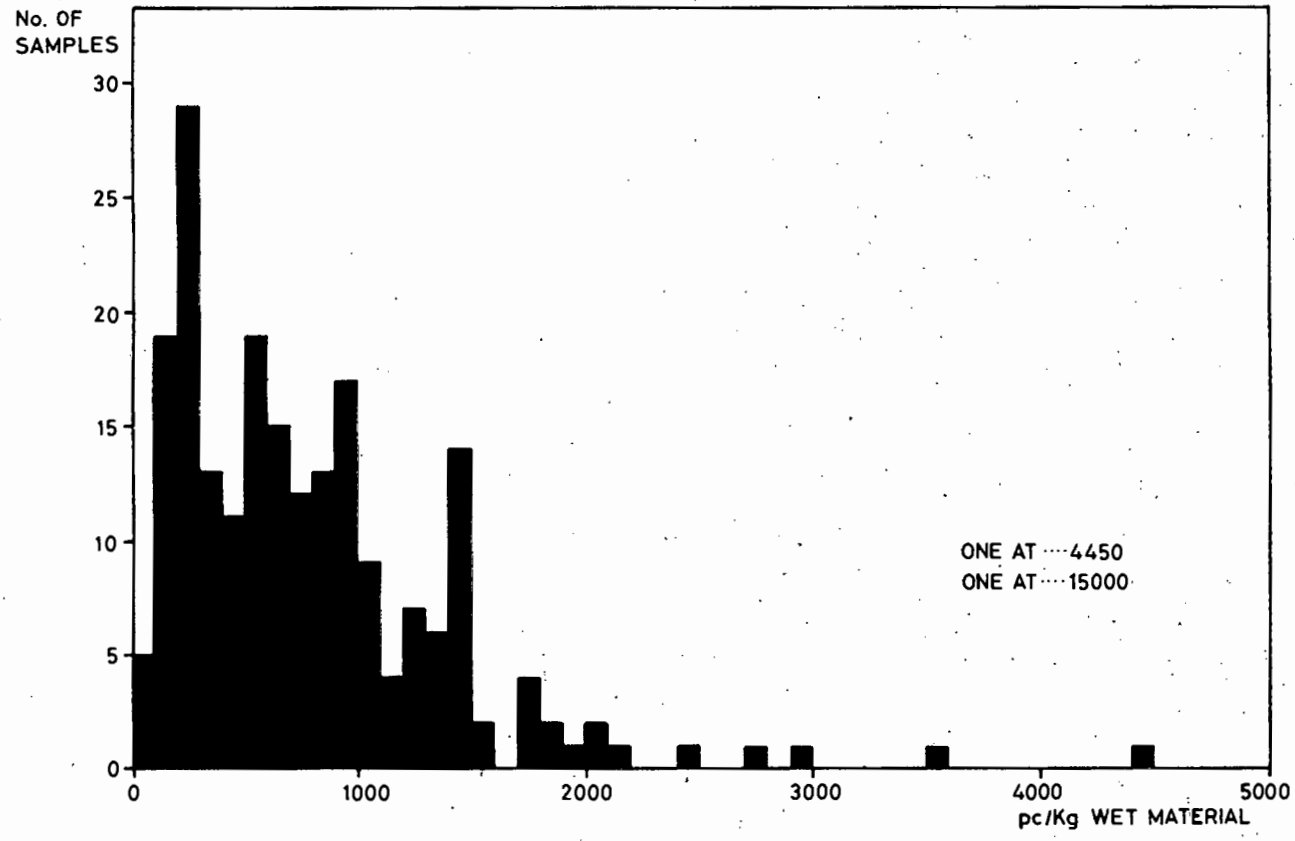

FIG. 3 FREQUENCY DISTRIBUTION OF TOTAL ACTIVITY IN WET ZOOPLANKTON

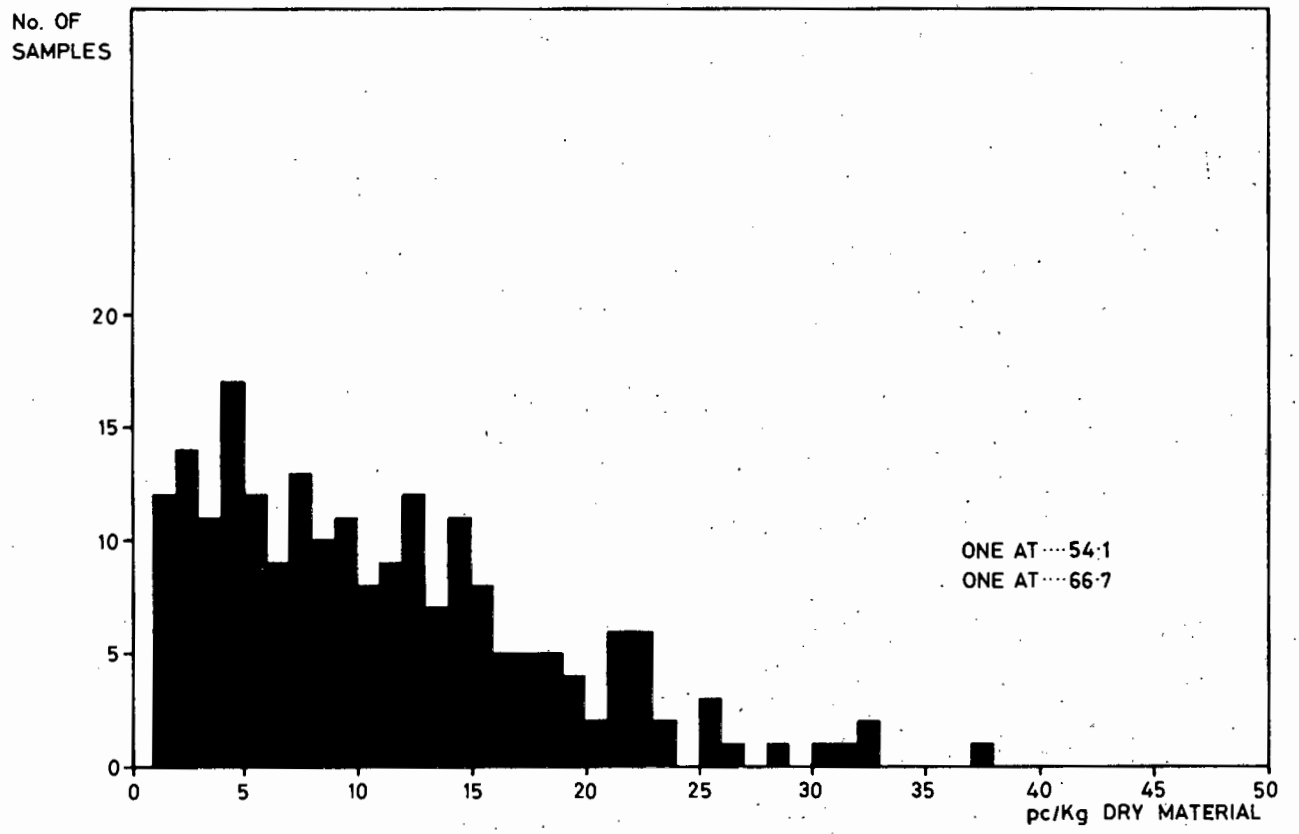

FIG. 4 FREQUENCY DISTRIBUTION OF TOTAL ACTIVITY IN DRY ZOOPLANKTON

lead-210 - polonium-210 pair becoming the principal source of skeletal radiation dose.

The alpha-activity of marine plankton is typically 1 pc/g wet material. The frequency distribution of 211 samples of zooplankton (Figs. 3 & 4) indicates that the most probable activity is between 200 and 300 pc/Kg wet material or 4-5 pc/g dry plankton. The characterisation of this activity as well as its dependence on species and oceanographic locality is discussed later.

2.3.2 Radiation Dosimetry

An evaluation of the contribution of alpha-activity to the total natural radiation dose received by marine organisms requires knowledge about the radiation dose received from external sources and the internal dose from natural beta emitters.

Most of the natural beta-activity in sea water is due to the nuclides potassium-40, rubidium-87 and carbon-14 (REVELLE and SCHAEFER, 1957). Of these nuclides the most important in terms of aboslute activity is potassium-40. In sea water the potassium concentration is 380 mg/l GOLDBERG 1963) and this value corresponds to approximately 300 pc/l of potassium-40. Rubidium-87 and carbon-14 account for a much smaller contribution viz. about 6 pc/l and 0.2 pc/l respectively (REVELLE and SCHAEFFER, 1957).

Data extracted from VINOGRADOV (1953) indicate that

the potassium content of fish, seaweed, molluscs and rock-lobster is 0.3%, 1.0%, 0.4% and 0.3% living material respectively. Owing to some uncertainty as to the potassium content of plankton, 17 zooplankton and 6 phytoplankton samples from various localities were analysed for potassium and rubidium. The mean concentrations of these respective elements in zooplankton were 5 600 p.p.m. and 2.6 p.p.m. dry material while in phytoplankton the levels were 4,000 p.p.m. dry material for potassium and 2.2 p.p.m. dry material for rubidium. Considering a mean wet/dry concentration factor of 16 for zooplankton and 21 for phytoplankton, the potassium contents of zooplankton and phytoplankton will correspond to 0.35 and 0.19 g potassium/Kg wet material respectively. Full details of the experimental technique and the results of the potassium and rubidium measurements on plankton are given in Section 10.7.

Owing to the low concentration of rubidium in marine organisms, coupled with the long half-life of rubidium-87, its contribution to the beta dose rate is negligible in comparison with radio-potassium. From the data given in the previous paragraph, plus the assumption that all the beta energy and half the gamma energy from potassium-40 decay is internally absorbed the following maximum internal dose rates due to this nuclide can be calculated.

TABLE 4 Maximum internal dose rates due to potassium-40.

Organism	Potassium Content (°/oo wet material)	*Max. Dose Rate millirem/yr
Zooplankton	0.35	3
Phytoplankton	0.19	1.6
Fish	3	25
Seaweed	10	84
Molluscs	4	34
Rock Lobster	3	25

*Considering the average beta energy = 0.5 MeV, gamma energy = 1.5 MeV and that the relative biological efficiency of beta and gamma rays is unity.

FOLSOM and HARLEY (1957) quote the radiations received by organisms in eleven radiological domains. The dose received by various marine organisms from external sources (predominantly cosmic radiation) is typically $\leq$ 40 millirads/yr near the sea surface and an order of magnitude lower at a depth of 100 m. As most of this dose is due to minimum ionizing radiations we may consider millirads/yr as being equivalent to the biological dose unit millirem/yr. Thus the maximum total radiation dose received by phytoplankton from external sources and internal potassium-40 will be little more than 40 millirem/yr. For fish it will be about 65 millirem/yr and for seaweed (non planktonic

algae) 124 millirem/yr.

The range of a typical alpha-particle in living plankton will be about 10-15 microns. If we consider a planktonic organism with dimension much larger than this figure, then to a good approximation, all the alpha-particles emitted by the organism will be absorbed internally provided that the activity is not distributed on the surface alone. In the latter case about one half or one third of the radiation would be internally absorbed. In general the dimension of individual zooplankters are typically 1000 microns or larger and provided the activity is not distributed on the surface area alone it is reasonable to assume that all the alpha-activity is internally absorbed. The same applies to larger organisms such as fish, molluscs, seaweed etc. In phytoplankton the position is more complicated. The dimensions of phytoplankton cells are very variable but typically the cell diameter is 10 microns and cell length anything up to 1000 microns. For purposes of this discussion we shall make the reasonable but nevertheless crude assumption that about 25% of the internally emitted alpha-particle energy is absorbed in living phytoplankters.

If we assume that the average alpha-particle energy is 5 MeV and that the relative biological efficiency (R.B.E.) of an alpha-particle is 10 (FEDOROV, 1965) then the internal radiation doses in the living organisms can be calculated from the <u>in vivo</u> specific alpha-activity.

In the calculations, the *in vivo* emanation problem (SPIERS, 1968) has been neglected. This is perhaps an oversimplification but little is known about the retention of radon in marine life. However, for zooplankton and fish, emanation may be neglected as most of the alpha-activity is due to unsupported polonium-210. In marine flora, in particular Agulhas phytoplankton, much of the alpha-activity is due to "residual" uranium series elements and the radiation doses received by these organisms will probably be lower than those given in Table 3 on account of an undetermined amount of radon emanation from the living organism. With the exception of phytoplankton, an alpha-activity of 10 pc/Kg living (wet) material corresponds to a biological radiation dose of 9.3 millirem/yr or to a good approximation the units of pc/Kg are equivalent to a dose of millirem/yr. In phytoplankton 10 pc/Kg living material corresponds to a dose of 2.3 millirem/yr. The internal alpha-radiation doses received by various marine organisms are given in Table 3.

The gross alpha-activities and radiation doses should be compared with similar measurements on foodstuffs of terrestrial origin. TURNER *et al.* (1958b) give the maximum alpha-activities in some human foods, and their results imply that the daily ingestion of alpha-activity from a typical western diet is likely to be less than 50 pc; probably about 20 pc. HILL (1965) considers that the daily intake of polonium-210 and lead-210 from

food contributes 1-10 pc of alpha-activity. If we consider the alpha-activities of the marine organisms given in Table 3 it is evident that some sea foods could contribute significantly to the ingestion of alpha-activity. Molluscs, which include abalone, oysters and mussels have a specific tissue activity of 1600 pc/Kg. Pelagic fish species are extensively used in the production of fish meal, and contain on the average 1300 pc of alpha-activity per Kg of wet material. Thus a daily human intake of only 100 g of wet shell fish or pelagic fish (about 30 g dry material) could conceivably increase the radioactivity ingested by man by an order of magnitude. The flesh of white demersal fish and rock-lobsters (about 150 pc/Kg wet material) have relatively low alpha-activities and are comparable with the levels in the livers of herbivorous ungulates (TURNER et al. 1958b; CHERRY et al. in press), but are nevertheless much higher than the levels in the flesh of herbivores. Most of the fish eaten in South Africa is white demersal fish, in particular the South Atlantic hake Merluccius capensis. The contribution to the activity ingested in the average South African diet from this fish however will be negligible.

The alpha-radiation doses received by marine organisms should be compared with the total skeletal dose in man. EISENBUD (1963) and HOLTZMAN (1966) have estimated that man receives a skeletal dose of 130 millirem/yr. All the

It should be pointed out that this organ of the rock-lobster is regarded as a delicacy and is widely used locally in the preparation of the sauce for garnishing the lobster flesh.

It is evident from the data presented that alpha-activity contributes the major fraction of the radiation dose in marine organisms. This is true even if a R.B.E. of as low as 4 (c.f. HOLTZMAN, 1966) is used for alpha-particles in biological tissues. The total alpha-radiation doses should be compared with the total natural doses from other radiation sources, which with the exception of sea weed are typically less than 75 millirem/yr.

The alpha-radioactivity in general increases down the food chain in the sequence:

sea water - phytoplankton - zooplankton - pelagic fish.

It follows that a logical step would be to investigate the activity in fish eating seabirds and also in battery chickens which are fed to a large degree on fishmeal.

In concluding this chapter it is worth restating that marine organisms have an alpha-activity typically higher than most forms of terrestrial life. The radiation doses received by marine organisms from internal alpha-activity indicate that marine life can in fact be considered as a relatively radioactive form of life. The implications are far reaching, for, as future generations will have to turn progressively to the sea for food, alpha-activity could conceivably become the major contributor to the skeletal radiation dose in man.

3. THE ALPHA-SPECTRUM IN MARINE LIFE

As is clear from Chapter 2 limited data on radium-226 and polonium-210 are available, but little else has been published on the other alpha-emitting nuclides in marine life. SHANNON and CHERRY (1967) showed that unsupported polonium-210 accounted for a large proportion of the gross alpha-activity in plankton, and this observation was subsequently confirmed by BEASLEY et al. (1969) for various marine organisms and protein concentrates. There is some uncertainty as to the radium content of plankton (e.g. SZABO, 1967). It is not clear from some of the published radium-226 concentrations in plankton whether the materials analysed were zooplankton or phytoplankton, but nevertheless it does appear that the radium-226 content of phytoplankton is two orders of magnitude higher than that of zooplankton.

Three main disequilibria in the uranium and thorium series in marine life can be expected. (i) In the uranium series, uranium-234, thorium-230 and radium-226 have half-lives which are long on an oceanographical time scale, and there is no reason to suppose these nuclides and uranium-238 will be accumulated to the same degree by marine life. From the published data on uranium and radium in marine organisms it does seem as though radium-226 is present in excess of its equilibrium concentration by two orders of magnitude. (ii) Below radium-226, a disequilibrium is to be expected on account of the

lead-210 - polonium-210 situation. The in vivo degree of equilibrium in this portion of the uranium series is uncertain, and is further complicated by the fact that both lead-210 and polonium-210 are introduced into the sea by precipitation in addition to natural decay of radium-226. (iii) In the thorium series, a large disequilibrium has been reported between thorium-232 and thorium-228 and it is likely that this disequilibrium may exist in plankton and pelagic fish. The radium-228 to thorium-228 disequilibrium has also been studied recently.

As a first step towards obtaining information on the alpha-spectrum in plankton a large capacity ion chamber was used, thus making it possible to confirm the alpha-disequilibria. Unfortunately limitations imposed by the background and resolution of the chamber made it impossible to run relatively low activity samples such as fish flesh, and thus the ion chamber data are slightly unrepresentative insofar as they are biased towards the "hotter" samples.

Details about the operation of the ion chamber and the interpretation of the results follow.

3.1 Ion Chamber Operation

The ion chamber used was identical in most respects to that designed by HILL (1961). The main advantage of this chamber is the large source area (1.5 m^2) which makes possible alpha-spectrometric analysis without pior chemical

concentration. The chamber itself is described in detail in Section 10.2.2, while its operation as well as the preparation of the source is described below.

In the preparation of a thin source, the material should ideally have a particle size of a micron or less and be spread uniformly over the face of the aluminised cellulose acetate sheet which forms the source area (see Section 10.2.2). Larger particle sizes or clusters of particles lead to excessive self-absorption. In order to achieve small particle sizes prolonged grinding is necessary, but owing to the fibrous nature of dried plankton it was not possible to achieve sub-micron size.

Approximately 0.1 - 0.5 g of dried sample was finely ground by means of a mortar and pestle to a particle size of about 10 microns or smaller. This material was then transferred to a clean polythene bottle to which 50 ml of double distilled water and four drops of Teepol had been added, and it was then shaken for ten minutes. The suspension was subsequently sprayed onto the aluminised cellulose acetate film by means of a modified perfume atomiser coupled to a blow bulb, and the water was evaporated off my means of a heater-fan. It was necessary to repeat the spraying and drying technique about three times until all the sample solution was deposited. It was found that this together with the use of Teepol avoided the formation of large droplets and puddles. An effective source area of 15,000 cm^2 is provided (see Section 10.2.2).

The cellulose acetate sheet (Section 10.2.2) was fitted and attached to a cylindrical perspex frame by means of cellulose adhesive tape. The frame was then placed inside the main chamber, the various electrical connections made and the door of the ion chamber closed and sealed.

The chamber was pumped down by a large capacity rotary pump to circa 180 μHg. The argon-methane counting gas was then fed into the chamber until a pressure of 1 cm Hg above atmospheric was reached (to facilitate the detection of possible leaks). The gas was circulated through the system by a second pump for a day and periodic checks made with the test sources (Pu-239, U-238, U-234) to ensure that their positions in the spectrum remain stable.

A four minute test source run was then made and the test sources turned out of the active counting volume. The main sample was allowed to run for about 50 hours after which time a further calibration run was made to check for any possible shift in the spectrum position.

The background blank runs were made regularly by performing runs using blank aluminised cellulose acetate. Thus it was possible to correct all data for the contribution from the sheet material and for emanation contribution from the chamber. Spectra of typical background and calibration runs are given in Figs. 5 and 6.

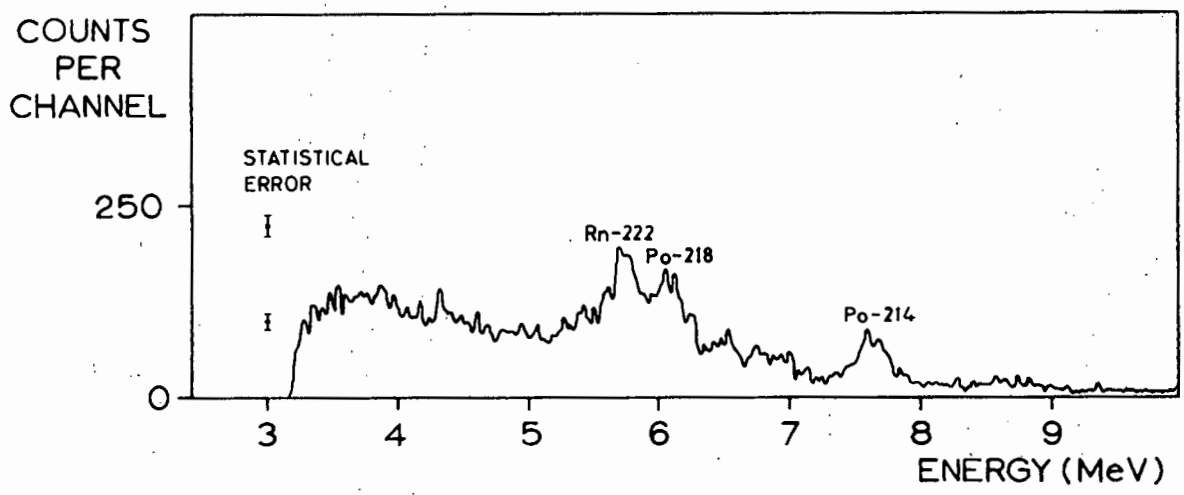

FIG. 5 ION CHAMBER - BACKGROUND
BLANK RUN - 50 HRS.

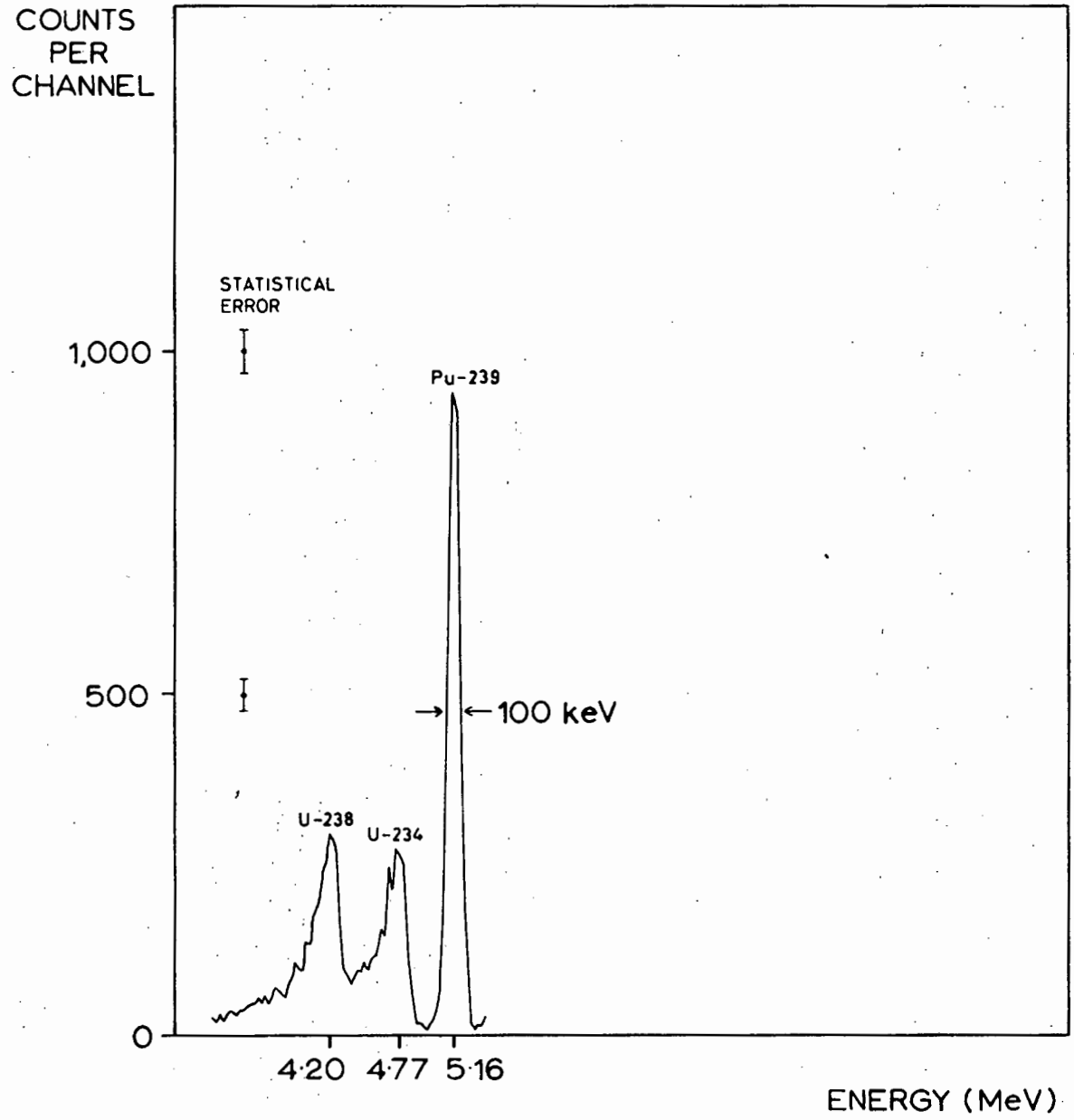

FIG. 6 ION CHAMBER - 4 MINUTE TEST
SOURCE RUN

3.2 Characterisation of the Activity

Several relatively "hot" dried plankton samples were run on the ion chamber and the alpha-spectra of seven of these are shown in Figs. 7-13. It is not possible to compare directly total ion chamber counts with absolute alpha-activities for two reasons. Firstly varying quantities of sample (0.1 - 0.5 g) were used and precise determination of the amount of material sprayed onto the sheet was not practical. Secondly, due to the circulation of the counting gas not all the radon-222 will decay in the sensitive volume of the chamber. The counts in the radon-222 and daughter peaks will in consequence be typically 50% of the radium-226 counts.

The alpha-spectra of zooplankton samples 17 and 16 are shown in Figs. 7 and 8 respectively. These figures are typical of zooplankton spectra and it is evident that the bulk of the alpha-activity is due to unsupported polonium-210. In sample 16 the spectrum indicates that radium-226 and short lived daughters account for the remainder of the activity while in sample 17 some radium-226 and thorium series activity may be present. Results from total alpha-counting of the corresponding samples are given in Table 5. (The "uranium series" is the residual activity after deducting the thorium series and unsupported polonium-210 activities from the gross alpha-activity). From these a thorium series activity of less than 1 pc/g dry material is indicated viz. - too low to be detected

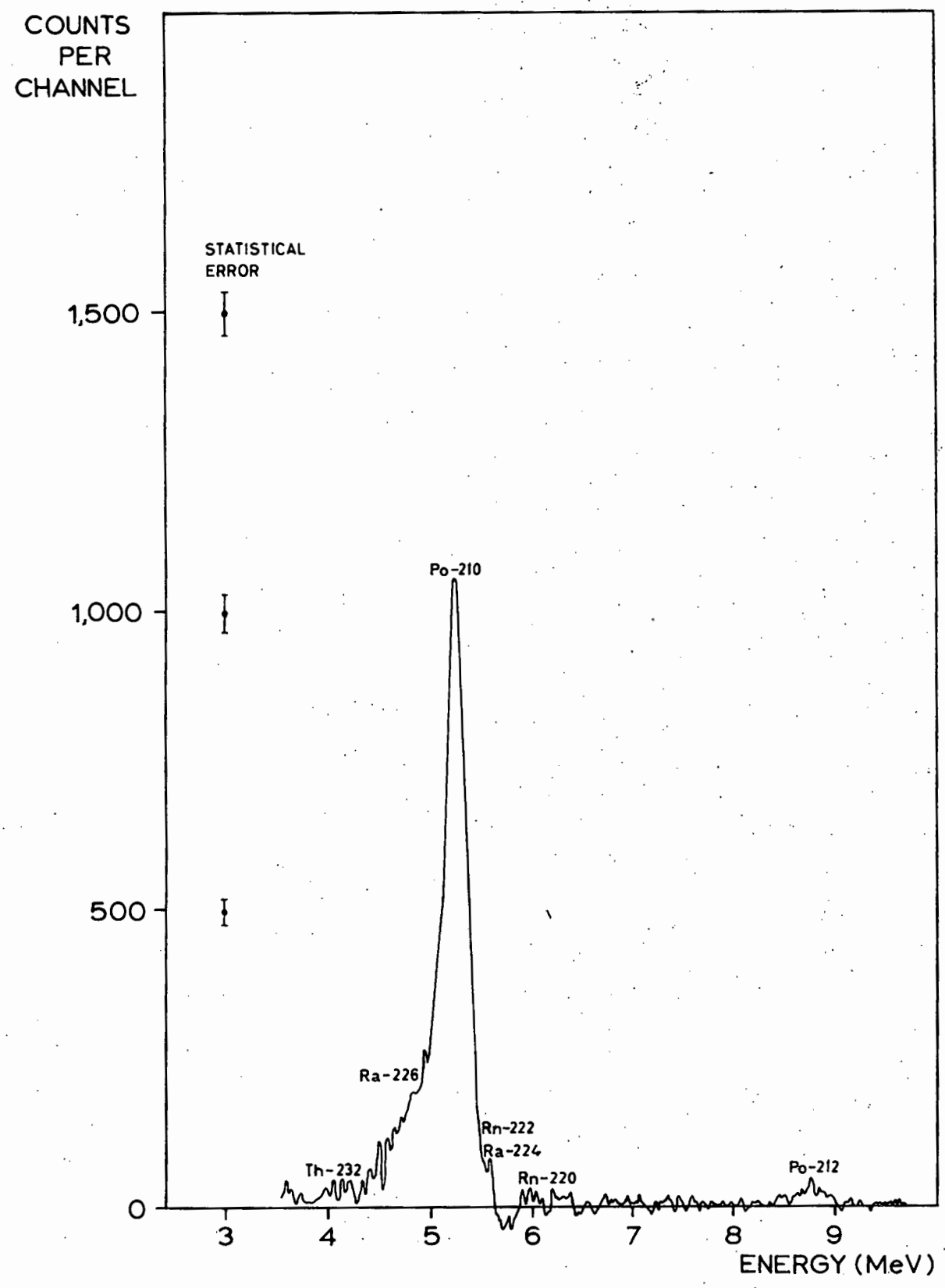

FIG. 7 ION CHAMBER ALPHA-SPECTRUM
SAMPLE 17 -50 HRS.

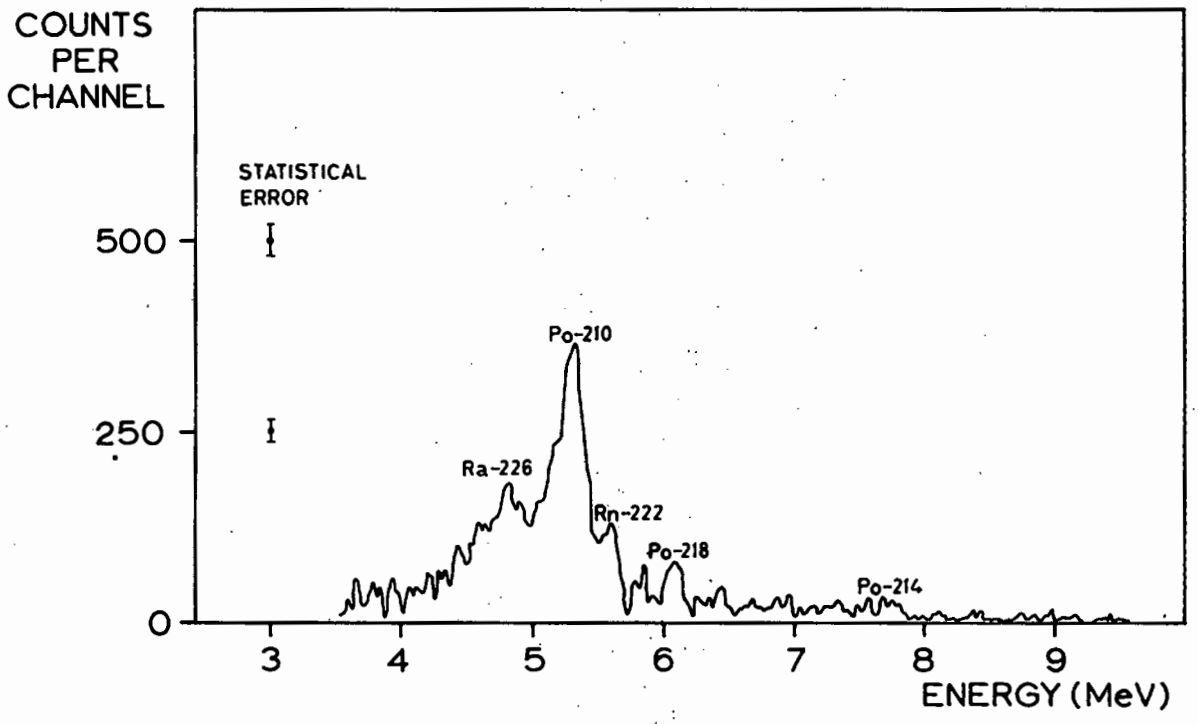

FIG. 8 ION CHAMBER ALPHA-SPECTRUM
SAMPLE 16 -50 HRS.

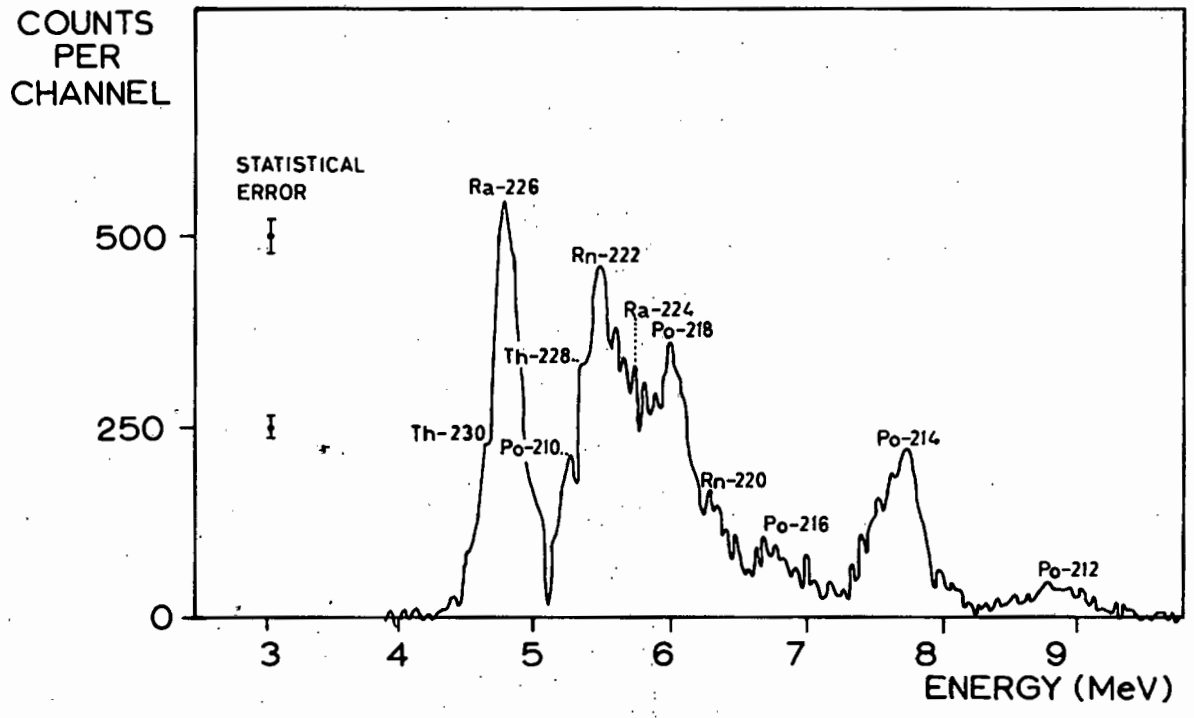

FIG. 9 ION CHAMBER ALPHA-SPECTRUM
SAMPLE 214 -50 HRS.

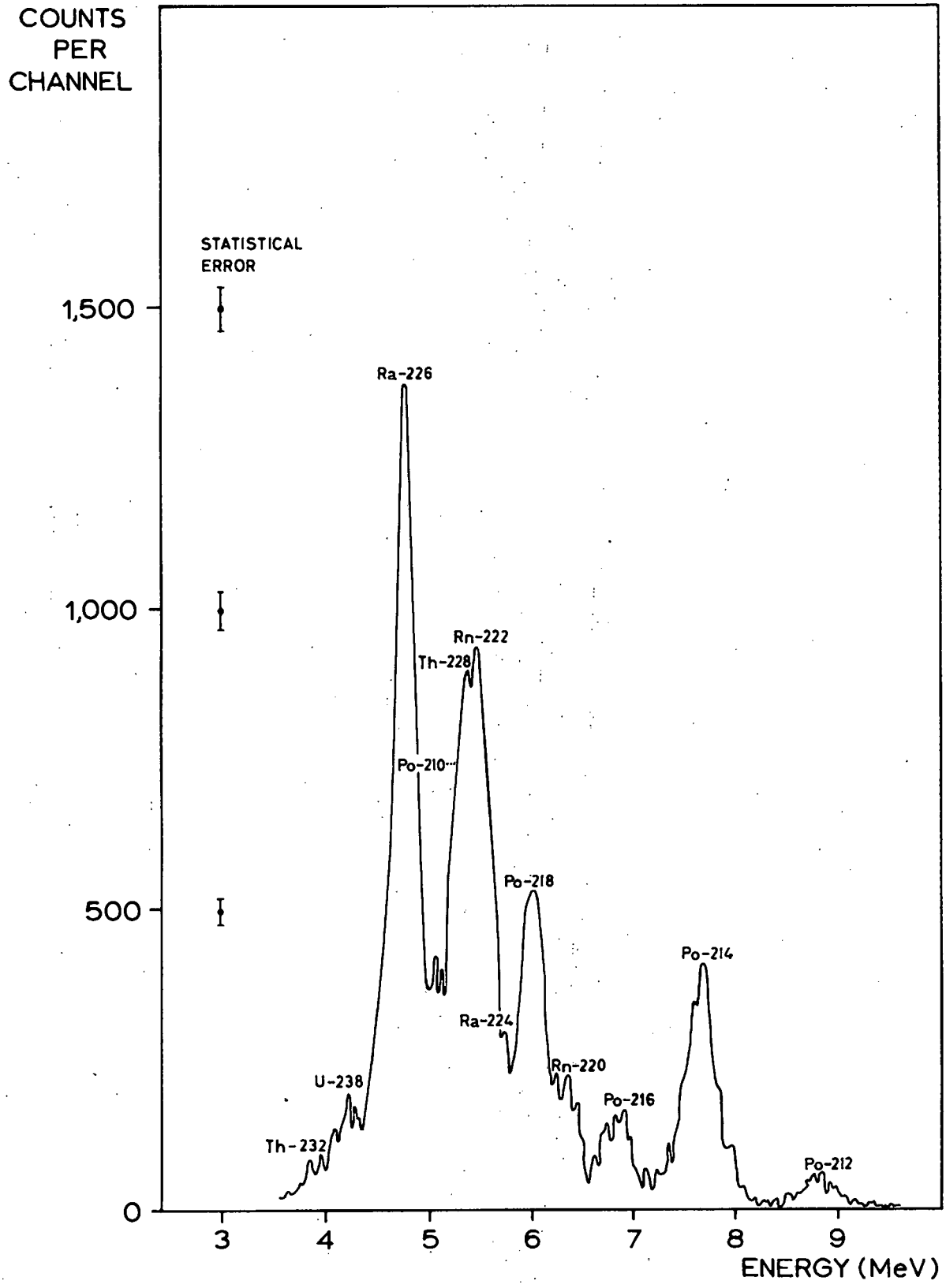

FIG.10 ION CHAMBER ALPHA-SPECTRUM
SAMPLE 213 -50 HRS.

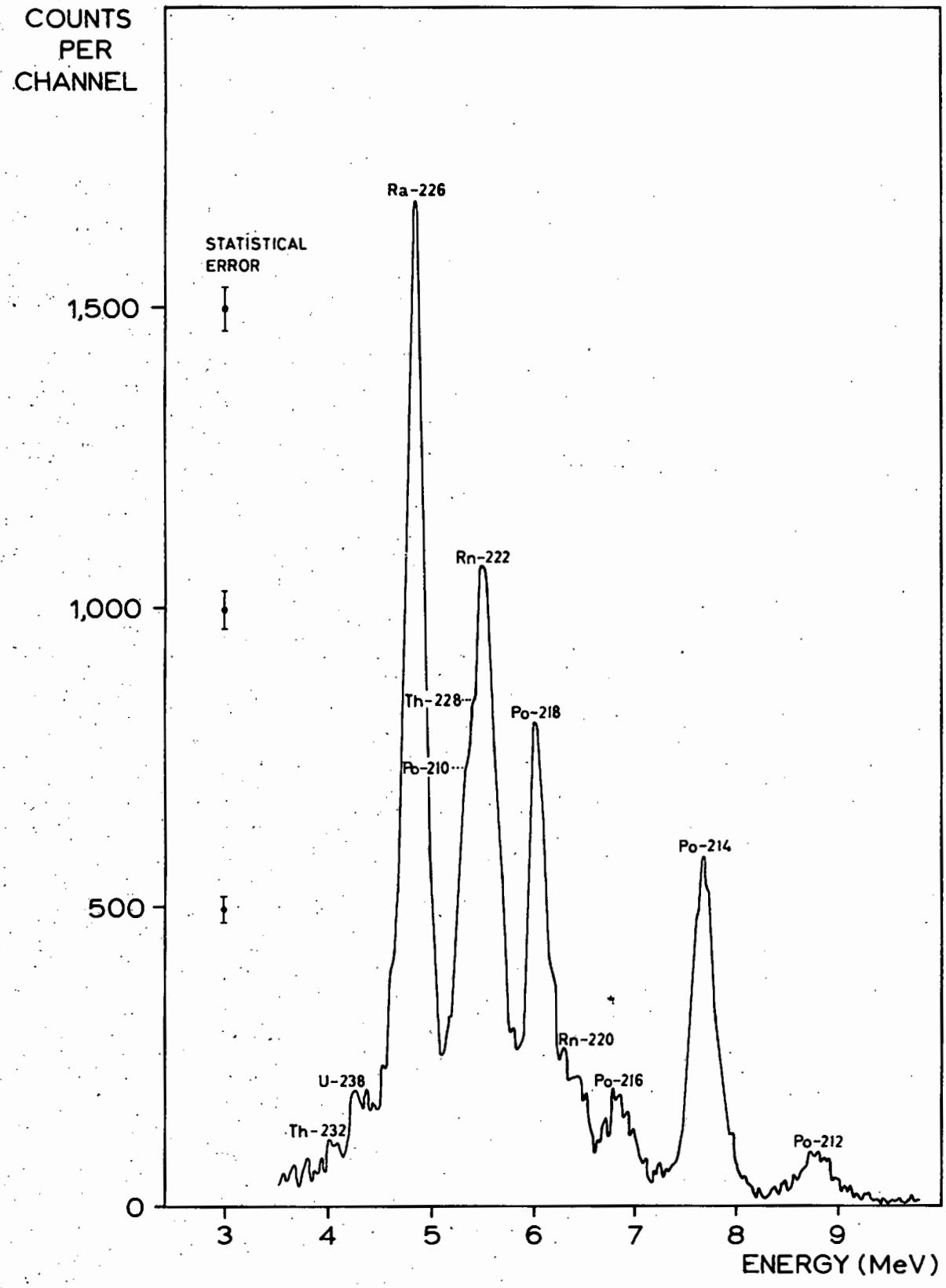

FIG.11 ION CHAMBER ALPHA-SPECTRUM
SAMPLE 215 -50 HRS.

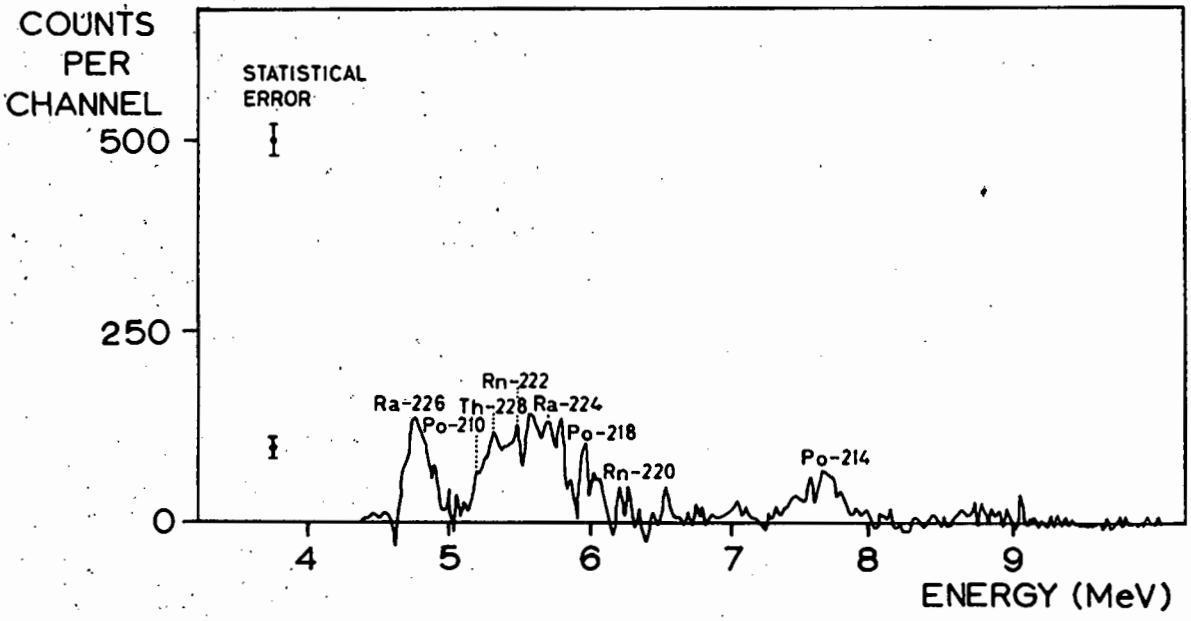

FIG. 12 ION CHAMBER ALPHA-SPECTRUM
SAMPLE 212 -50 HRS.

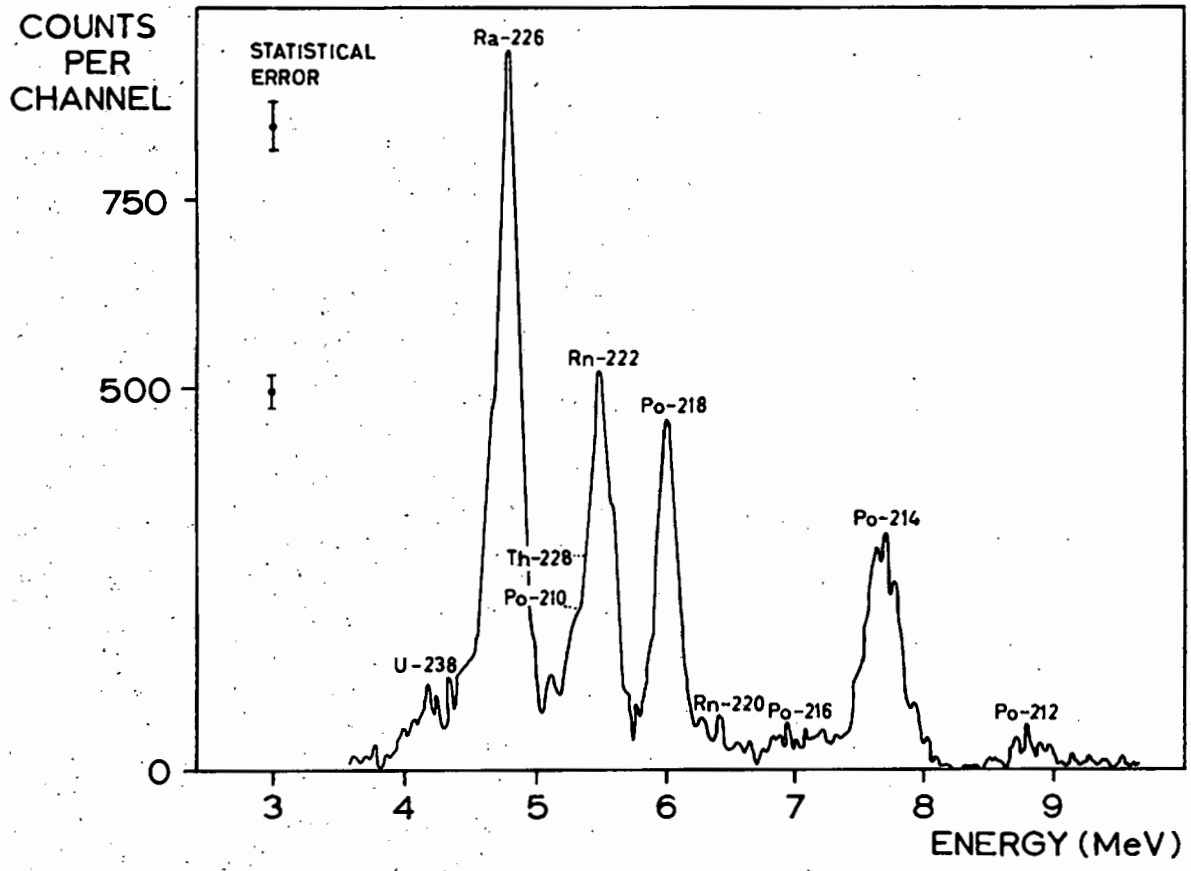

FIG. 13 ION CHAMBER ALPHA-SPECTRUM
SAMPLE 221 -50 HRS.

with any degree of certainty on the ion chamber. Unsupported polonium-210 accounted for more than 90% of the activity of sample 17 and about 80% of sample 16. These results are in good agreement with the ion chamber characterisation.

TABLE 5 Corresponding Total Alpha-Counting Results

Sample Number	"Uranium series" pc/g (dry)	Thorium series pc/g (dry)	Excess polonium-210 pc/g (dry)
16	3.2 ± 2.5	0.83 ± 0.41	15.7 ± 2.2
17	2.1 ± 3.5	0.95 ± 0.52	29.5 ± 3.0
212	36.9 ± 2.7	3.19 ± 1.08	not detected
213	53.5 ± 4.4	13.9 ± 4.3	not detected
214	74.3 ± 3.0	8.8 ± 1.1	not detected
215	75.9 ± 5.6	12.7 ± 5.5	not detected
221	175 ± 5	uncertain	not detected

Five phytoplankton spectra are given in Fig. 9-13. Four of these samples were collected in the Agulhas Current while one (221) was collected about 120 miles north-west of Cape Town. Two features are immediately evident from the ion chamber spectra. Firstly radium-226 and short lived daughters are the main contributors to the alpha-activity; secondly thorium series members contribute to about 5 - 10% of the activity. The corresponding total alpha-counting data are given in Table 5, and are again compatible with the conclusions drawn from the ion chamber

data.

Three of the phytoplankton spectra (Figs. 10, 11 and 13) had a small peak corresponding to an energy of about 4.2 MeV. It seems highly probable that this is due to uranium-238, and this being so it would imply that the radium-226/uranium-238 activity ratio in phytoplankton is about 20. This figure is to be compared with corresponding ratios of 250 in fish flesh, 0.3 in shells and 0.13 in sea water calculated from data given by various authors (e.g. ATEN et al. 1961; HOLTZMAN, 1969; KOCZE and TITZE, 1958; SZABO, 1967).

Inflections corresponding to an energy of 4.7 MeV on the radium-226 peaks in three of the spectra (Figs. 9, 11, and 13) would seem to indicate the presence of thorium-230. The inflection (step) is particularly evident at 4.7 MeV in Fig. 9 (sample 214).

Daughters of thorium-228 (e.g. radon-220, polonium-216, polonium-212) are evident in four of the phytoplankton spectra (Figs. 9, 10, 11 and 13). Thorium-228 and radium-224 are overshadowed by the large radon-222 peak in which the resolution is poor, but nevertheless bumps on this peak correspond to energy of the thorium-228 alpha. Thorium-232 was generally not detected although there may be some evidence for it in Figs. 10 and 11. It is clear however that thorium-228 is present in excess of its alpha-parent by a factor about five or more.

A feature of all the phytoplankton spectra is that

polonium-210 appears to be present at levels slightly less than equilibrium values with radium-226. Unfortunately the spectra give no information about lead-210. Although unsupported polonium-210 has been detected in numerous phytoplankton samples by total counting it was not detected in the "hot" samples by this technique. SHANNON and CHERRY (1967) reported unsupported polonium-210 at levels of about 3 pc/g in dry phytoplankton. In "hot" samples such relatively low unsupported polonium-210 activity levels would not easily be detected by total counting.

To summarise therefore it appears from the ion chamber data that:

(a) Excess alpha-unsupported polonium-210 accounts for most of the alpha-activity in zooplankton.

(b) Radium-226 and daughters and thorium series elements account for the remainder of zooplankton alpha-activity.

(c) Radium-226 and daughters account for much of the activity in the "hot" phytoplankton.

(d) Thorium-228 and daughters contribute typically 5-10% to the alpha-activity of the "hot" phytoplankton samples while thorium-230 is present is some of the samples.

It seems that investigation of the following radio-elements in the marine environment is of particular importance:

(1) Radium-226 and radium-228. In the following section of this chapter the total alpha-counting data and the ion chamber data already presented will be used in order to obtain an estimate of radium-226 in marine life.

(2) Polonium-210 and lead-210. Data on their occurrence in marine life (mainly plankton) and sea water will be reported in Chapter 4.

(3) Thorium series elements and the thorium-228/thorium-232/thorium-230 activity ratios. Chapter 5 presents data on these in plankton.

3.3 Radium-226 in Marine Life

From the foregoing discussion it is evident that, excluding the polonium-214/lead-210/polonium-210 disequilibria, radium-226 is the effective head member of the uranium series in zooplankton and phytoplankton. After deducting thorium series and excess polonium-210 activities from the total alpha-activity, the radium-226 concentration can be calculated approximately from the "uranium series" or "residual" activity. This is done as follows.

In the thirteen zooplankton samples analysed for lead-210 the mean lead-210 to residual uranium series activity ratio was 0.25. This residual activity is due essentially to radium-226 and its daughters i.e. radium-226 plus three alphas (radon-222, polonium-218 and polonium-214,

which will be in equilibrium with radium-226 in the sample counted by the total alpha-technique) plus that fraction of the polonium-210 which is supported by lead-210. Use of the ratio 0.25 quoted above then indicates that radium-226 constitutes, on the average, 0.19 of the residual activity. Similarly, for four "cool" phytoplankton samples the mean lead-210 to residual alpha-activity ratio was 0.17, and by the same argument as for zooplankton, it is seen that radium-226 constitutes, on the average 0.21 of the residual activity. For "hot" (i.e. residual activity greater than 10 pc/g dry material) phytoplankton samples, no lead-210 measurements were available, but data extracted from the ion chamber results, allowing for the emanation disequilibrium, indicated that radium-226 accounted for, on the average, 0.22 of the residual activity in these samples. It is seen that the multiplicative factor used in the calculations varies between 0.19 and 0.22 for the three sample categories, and it therefore seems likely that the uncertainty introduced will not be in excess of 15%.

The radium-226 concentrations in 35 phytoplankton samples are given in Table 6.

For the purpose of discussion the phytoplankton samples from the Agulhas Current are considered separately from the others owing to their characteristically higher radium-226 concentrations. The mean (excluding sample 221, marked with asterisk) radium-226 content of 1.0×10^{-12}g

TABLE 6 Radium-226 in Phytoplankton

Agulhas Current		W. Coast and Oceanic	
Sample Number	Radium-226 (10^{-12} g/g dry plankton)	Sample Number	Radium-226 (10^{-12} g/g dry plankton)
212	8.1 ± 0.6	218	0.5 ± 0.1
213	11.8 ± 1.0	219	0.1 ± 0.8
214	16.3 ± 0.7	220	1.1 ± 0.2
215	16.7 ± 1.2	221*	38.5 ± 1.1
216	3.1 ± 1.0	222	1.2 ± 0.1
217	3.5 ± 1.0	223	1.3 ± 0.1
225	1.4 ± 0.2	224	1.5 ± 0.2
233	11.2 ± 0.6	226	2.5 ± 0.3
234	1.1 ± 0.2	227	0.5 ± 0.1
235	3.5 ± 0.2	228	4.8 ± 0.8
		229	0.6 ± 0.5
		230	Not detected
		231	0.3 ± 0.4
		232	0.7 ± 0.5
		236	0.6 ± 0.2
		237	1.7 ± 0.8
		238	0.3 ± 0.1
		239	0.5 ± 0.1
		240	1.5 ± 0.1
		241	0.4 ± 0.1
		242	1.4 ± 0.1
		243	0.6 ± 0.1
		244	0.8 ± 0.1
		245	1.0 ± 0.1
		246	0.7 ± 0.9

Ra-226/g dry material in West Coast and oceanic phytoplankton agrees closely with values of about 2×10^{-12} g Ra-226/g dry material obtained by FÖYN et al.(1939) and KOCZY and TITZE (1958). The mean radium concentration in phytoplankton, collected during various cruises into the Agulhas Current was 7.7×10^{-12} g Ra-226/g dry material, i.e. almost an order of magnitude higher than in the other samples. The West Coast and oceanic samples comprised several bloom genera (e.g. Skeletonema, Nitzschia) while various Chaetoceros and Rhizosolenia spp. accounted for a large portion of the Agulhas Phytoplankton samples. The highest radium-226 viz. 38×10^{-12} g Ra-226/dry material was recorded in sample 221 which was collected on the West Coast during December 1967. This sample contained mainly the diatom Rhizosolenia alata formgracillima, a warm water species. It is possible that this sample may be associated with the component of mixed Agulhas Water which penetrates into the West Coast about 100 miles off shore during the summer (SHANNON, 1970), but positive evidence is lacking. It is interesting to note that CHERRY (1964) recorded the highest gross alpha-activity (95 pc/g dry material) in a sample of Rhizosolenia hyalina (Ostenfeld) collected in the Agulhas Current during 1958.

NOTE: In calculating averages for West Coast phytoplankton in this and in following chapters, sample 221 has been omitted as it is not considered as being representative of the West Coast region.

The residual activity in zooplankton is much lower than in phytoplankton. Concentrations ranged from "zero" to 1.8×10^{-12} g Ra-226/g dry material but individual results were not very meaningful owing to the relatively high statistical errors of the residual activities. The mean radium concentration in 211 zooplankton samples derived from the residual activity was however 0.3×10^{-12} g Ra-226/g dry plankton, a figure somewhat lower than in phytoplankton but about three times higher than the mean given by SZABO (1967) viz. 8.4×10^{-14} g Ra-226/g dry material for seven zooplankton samples from the Bahamas.

For comparison the mean radium content of algae (sea weed), mollusc shells and crustacean shells has been calculated on the assumption that radium-226 accounted for 20% of the residual alpha-activity. It should be emphasised that no alpha-spectra have been obtained for these samples and the data for the same given in Table 7 should accordingly be regarded as somewhat speculative.

The radium-226 contents of zooplankton and Agulhas phytoplankton expressed <u>in vivo</u> were 25×10^{-12} and 365×10^{-12} g Ra-226/kg wet material respectively. Using the usually quoted R.B.E. for alpha-particles of 10, it follows that from radium-226 <u>alone</u> zooplankton and Agulhas phytoplankton receive radiation doses of 21 millirem/yr and 81 millirem/yr respectively. Taking into consideration the short lived daughters of radium, the <u>effective</u> radiation dose received from this nuclide may

TABLE 7 Mean Radium-226 Concentrations in Marine Organisms: Number of samples in brackets. (errors are standard errors of the mean)

Organism	Radium-226 (10^{-12} g/g dry material)	Radium-226 (10^{-12} g/Kg wet material)
Agulhas (10) Phytoplankton	7.67 ± 1.85	365 ± 88
Other (24) Phytoplankton	1.02 ± 0.14	56 ± 8
Zooplankton(211)	0.30 ± 0.02	24 ± 2
Algae (13) (sea weed)	0.21 ± 0.03	29 ± 4
Mollusc (15) shells	0.06 ± 0.02	51 ± 17
Crustacean(14) shells	0.15 ± 0.03	69 ± 16

be much higher. These dose rates are, in any event, considerably higher than the internal dose received from the natural beta emitters (< 3 millirem/yr for zooplankton, < 1.6 millirem/yr for phytoplankton - see Chapter 2) and doses received from external sources, and should be compared with total dose rates of 120 - 140 millirem/yr received by human body tissues (EISENBUD, 1963; HOLTZMAN, 1966).

The high radium concentrations in some of the phytoplankton samples present an intriguing problem. It is perhaps worth mentioning that CHERRY et al. (1969) found high thorium-228 concentrations in Agulhas plankton and

from data presented in Chapter 5 it is certain that this thorium activity was in part at least supported by radium-228. Furthermore the radium-226 content of zooplankton collected simultaneously and at the same stations as the Agulhas phytoplankton had a mean radium content of 43×10^{-12} g Ra-226/kg wet material, i.e. almost twice the mean value of all the zooplankton samples. Thus, if the radium-226 content in the upper mixed layer in the Agulhas Current is taken as 5×10^{-14} g/l, then plankton species associated with this current accumulate radium to a far greater degree than plankton from other regions, the concentration factors being 7,300 and 860 for the phytoplankton and the corresponding zooplankton respectively. Although the zooplankton samples collected at same stations as the "hot" Agulhas phytoplankton had a higher than average radium content, zooplankton samples collected at other localities in the Agulhas Current contained radium at levels identical to the mean value for zooplankton. This implies therefore that the higher radium content of zooplankton collected at stations where phytoplankton blooms occurred was a result of the zooplankton grazing on the "hot" phytoplankton rather than direct uptake from seawater. However it is just possible that surface Agulhas Water may be enriched in radium due to upwelling associated with the dynamics of this rapidly flowing current system. SHANNON et al. (1970) noted that Agulhas Water was enriched in polonium-210 compared with

Subtropical Surface Water. A detailed investigation of radium in the Agulhas Current would be required to confirm the above hypothesis.

Using recent data and making various assumptions SZABO (1967) calculated that the residence half-life of radium in sea water was 940 years. He considered a carbon production rate of 5.5×10^{-3} g carbon/cm^2/yr and assumed that carbon comprised 30% of dry plankton. Further assumptions were that 10% of the average yearly production represented the standing crop and that 10% of the average yearly production was lost to the deep water layers. However, the plankton radium concentrations used by SZABO (1967) were based on measurements on zooplankton, not phytoplankton, which as has been shown above have a considerably higher radium content. Following an argument similar to Szabo's and taking the radium-226 content of Agulhas phytoplankton and water as 7.7×10^{-12} g Ra-226/g dry material and 5×10^{-14} g/l respectively then residence half-life of radium-226 in the Agulhas Current would be about 25 years.

It is proposed however to follow a slightly different argument. Numerous measurements (unpublished) made by the Division of Sea Fisheries on particulate matter in the surface layer around South Africa indicate that the organic content of the surface layer is about 2 mg (dry) per litre, and that the corresponding carbon content is about 25% of this, or about 0.5 mg/litre. Let us consider the surface layer as being the upper 100 m. The carbon

content of this water column corresponds to 5×10^{-3} g Carbon/cm^2.

Productivity measurements made around South Africa by STEEMANN NIELSEN and JENSEN (1957) indicated a productivity of about 0.4 gC/ m^2/day. This is equivalent to a production rate of 1.5×10^{-2} gC/cm^2/yr, and this value should be compared with the standing crop of 0.5×10^{-2} gC/cm^2 for the upper 100 m (see above). Whereas SZABO (1967) assumed that the annual removal was equal to the <u>standing crop</u>, it is considered more reasonable to assume that the organic matter removed from the surface layer per year is equal to the <u>production</u>. Thus if this organic matter (dry) contains 25% carbon, then the amount of matter removed will = $\frac{100}{25} \times 1.5 \times 10^{-12} = 6 \times 10^{-2}$ g dry matter/ cm^2/yr.

Further if this organic matter is assumed to contain radium at similar levels to phytoplankton, then the biological removal of radium-226 from the surface layer of the Agulhas Current would be $7.7 \times 10^{-12} \times 6 \times 10^{-2} = 46 \times 10^{-14}$ g Ra-226/cm^2/yr. If inorganic removal is negligible compared with organic (biological) removal processes, then we may write

$$RN = 46 \times 10^{-14} \text{ g Ra-226/cm}^2\text{/yr}$$

where N is the concentration of radium-226 in the mixed layer, and R is the probability per unit time of a radium atom being removed biologically. R is termed the "rate

constant" and the reciprocal of R is customarily referred to as the (biological) removal time for the isotope concerned. Considering the radium-226 content of the surface layer as 5×10^{-14} g/l (viz. 5×10^{-13} g/cm^2 = N) and substituting above it is found that R = 0.9 years^{-1}. Thus the biological removal time for radium-226 from the surface layer of the Agulhas Current would only be about one year. For the West Coast and oceanic regions it can be shown to be about 8 years. The residence half-lives for radium-226 in these respective areas are 0.7 and 5.5 years. It should be emphasised that the seas around South Africa are highly productive regions, and consequently these rapid removal times may not apply to the World Ocean in general. If we follow the assumption of Szabo's that the removal of organic matter per year is equal to the standing crop, then removal times three times as long would result. Lower concentrations of organic matter and longer replacement times would result in corresponding longer residence and removal times. Although the above estimates are crude, being based on several assumptions, they nevertheless do imply that biological removal of radium-226 is much more important than radioactive decay as a mode of removal of this nuclide from the surface layer.

It would be logical to follow up this research with measurements of radium in particulate organic matter in order to verify the very rapid removal times as calculated from extrapolation of plankton data.

4. POLONIUM-210 AND LEAD-210 MEASUREMENTS

4.1 Sea Water

4.1.1 Development of method

From theoretical considerations, it was evident that the polonium-210 content of sea water would be extremely small and that one would be dealing with a micro-micro trace element. Polonium-210 is strongly adsorbed onto glass (FLYNN, 1968) and this necessitates a cautious sampling and storing procedure. Polonium-210 is extremely volatile at temperatures greater than about 200°C (MARTIN and BLANCHARD, 1969) and ideally extraction should be carried out at <120°C as rapidly as possible.

Polonium may be extracted from large volume water samples by using a scavenger such as ferric hydroxide (FOLSOM 1966), but this method was not considered feasible owing to difficulties associated with the sampling and suitable storage of a number of 50 litre samples. An attempt was therefore made to analyse the sea water for polonium-210 using solvent extraction on small samples.

Polonium has been separated by solvent extraction techniques using various chelators such as TTA, or by extracting the ion-association complex with chloride into tributyl phosphate-dibutyl ether mixtures (MORRISON and FREISER, 1957), among others (BRASTED, 1961) but separation has usually been emphasized rather than concentration.

Dr. M.J. Orren of the Geochemistry Department, University of Cape Town suggested that the diethyldithiocarbamate method of MORRISON and FREISER (1957) or the ammonium pyrrolidine dithiocarbamate method used successfully by himself for various trace metal determinations be tried. Initially, assuming that polonium would resemble its periodic table congenor tellurium in general properties, the diethyldithiocarbamate method used by MORRISON and FREISER (1957) to extract tellurium quantitatively at pH 8.5 was tested. Sea water spiked with polonium was treated with sodium diethyldithiocarbamate and extracted with carbon tetrachloride, but polonium was not extracted efficiently.

Since its synthesis by MALISSA and SCHÖFFMANN (1955) ammonium pyrrolidine dithiocarbamate (APDC) has been shown to form stable complexes with many elements over a wide pH range. Extraction of the APDC-metal chelates with methyl isobutyl ketone (MIBK) is a particularly useful technique combining the benefits of rapid, quantitative extraction over a wide pH range with minimum laboratory manipulation. The APDC/MIBK system has been extensively used as a preconcentration technique in atomic absorption analysis (MULFORD, 1966) and quantitative recoveries of metals such as copper and zinc, present at parts per billion (10^9) levels in sea water, were obtained with a single, one minute extraction step by ORREN (1967). The chemistry of polonium resembles that of bismuth and lead more closely than that of the group 6 elements (BRASTED

1961) and both bismuth and lead are extracted quantitatively with APDC/MIBK at pH 1-6 (MULFORD, 1966).

Extraction of polonium spikes with a 1% w/v APDC solution and MIBK was incomplete at pH 2, but increasing the APDC solution to 4% w/v increased the stability of the complex satisfactorily. The efficiency was further increased by a five minute rather than a one minute shaking period. MIBK is slightly soluble, and about 25 ml dissolves in a one and a half litre sample. ORREN (1967) found that, with copper and zinc, all the chelate remained in the separated organic layer, despite lowered recovery of solvent. This appears to be the case with polonium also.

Attempts to strip the organic layer with hydrochloric acid, in preparation for plating, failed as the acid and ketone phases did not separate, probably because of salt formation, and the solvent had to be evaporated off.

It was subsequently found that the method was almost as effective for the detection of lead-210 as well. The whole procedure was carried out at a pH of 2 or lower to minimise possible adsorption problems.

4.1.2 Experimental[†]

One and a half-litre sea water samples were collected at predetermined depths by means of a N.I.O. type plastic sampler. Samples were immediately run into specially prepared and volumetrically calibrated polythene bottles and rapidly frozen to -20°C in a large capacity plate freezer. Samples were stored at -20°C until they were analyzed. The polythene storage bottles were washed prior to use with concentrated hydrochloric acid followed by two washings with double glass-distilled water. Thirty ml of 11.7 N A.R. hydrochloric acid was added to each polythene bottle prior to the addition of the sea water sample to further minimise possible adsorption.

Samples were thawed rapidly prior to analysis, and the contents transferred into a glass beaker. The pH was then adjusted to 2.0 by the addition of A.R. ammonia solution. Care had to be taken not to overshoot pH 2.0 (which is close to the end point of the reaction). The solution was then immediately transferred to a 2 litre separating funnel and 15 ml of freshly prepared 4% APDC solution was added. The funnel was vigorously shaken for one minute, allowed to stand for five minutes and again shaken for one minute. Seventy five ml of solvent (MIBK) was added and the contents shaken for five

[†]Details of the technique as outlined in this Section are at present being published (SHANNON and ORREN, *Anal. Chimica. Acta* in press).

minutes after which it was left to separate out for thirty minutes. The aqueous portion was discarded and 6 ml of 11.7 N A.R. hydorchloric acid was added to the organic extract. After shaking, the latter was transferred to a glass beaker and evaporated nearly to dryness (i.e. to about 0.5 ml) on a hotplate (b.p.of MIBK is 114°-117°C).

The residue was dissolved by the addition of 10 ml 11.7 N A.R. hydrochloric acid. The polonium-210 was then plated out of the acid solution using the deposition cell and chemical technique of FLYNN (1968), the only difference being that teflon was substituted for perspex (the latter is attacked by small amounts of MIBK present in the plating solution).

After the first plating, the plating solution was retained and stored for two months in polythene bottles after which time it was again plated out. By allowing any lead supported polonium-210 to build up an estimate of the lead content was made (HILL, 1965; HOLTZMAN, 1969; BEASLEY et al. 1969). Statistics would have been considerably improved if samples had been stored for four months between platings instead of for two months.

The silver discs were packed on a zinc sulphide phosphor in a manner similar to that described by TURNER et al.(1958a) and used here previously (CHERRY 1964, SHANNON and CHERRY, 1967) the only difference being that the silver disc formed the material to be counted (see Section 2.2). This provided an individual sealed sample

phosphor system, thereby minimising the likelihood of contamination. Samples were counted on the conventional photomultiplier assemblies. The validity of the assumption that all the counts above background were in fact due to polonium-210 only was confirmed for all the sea water samples by subsequent counting of the silver discs on a multichannel alpha-spectroscopy semi-conductor detector system (see Section 10.2).

The background blank for the total counting technique was provided by performing solvent extraction and plating on a doubly-distilled water sample. This blank gave a count rate of 1.00 ± 0.05 counts per hour. Errors viven for all the samples are the standard deviations due to counting statistics only.

The efficiency of the solvent extraction method for polonium-210 was determined by the addition of lead-210 plus polonium-210 (in equilibrium) spikes ranging from 0.03 pc/l to 400 pc/l (Table 8). A linear calibration curve (Fig. 14) was obtained and the overall efficiency of the entire extraction and plating technique was 92%. Similarly an overall efficiency of 85% was obtained for the lead-210 determinations (Fig. 15). It appears that the solvent extraction stage is essentially quantitative, even at the extremely low concentration of polonium in sea water. (viz. at the level of 1 part in 10^{20} or 10^{21}!) This is possibly one of the lowest levels to which solvent extraction has been applied, and the ability of the

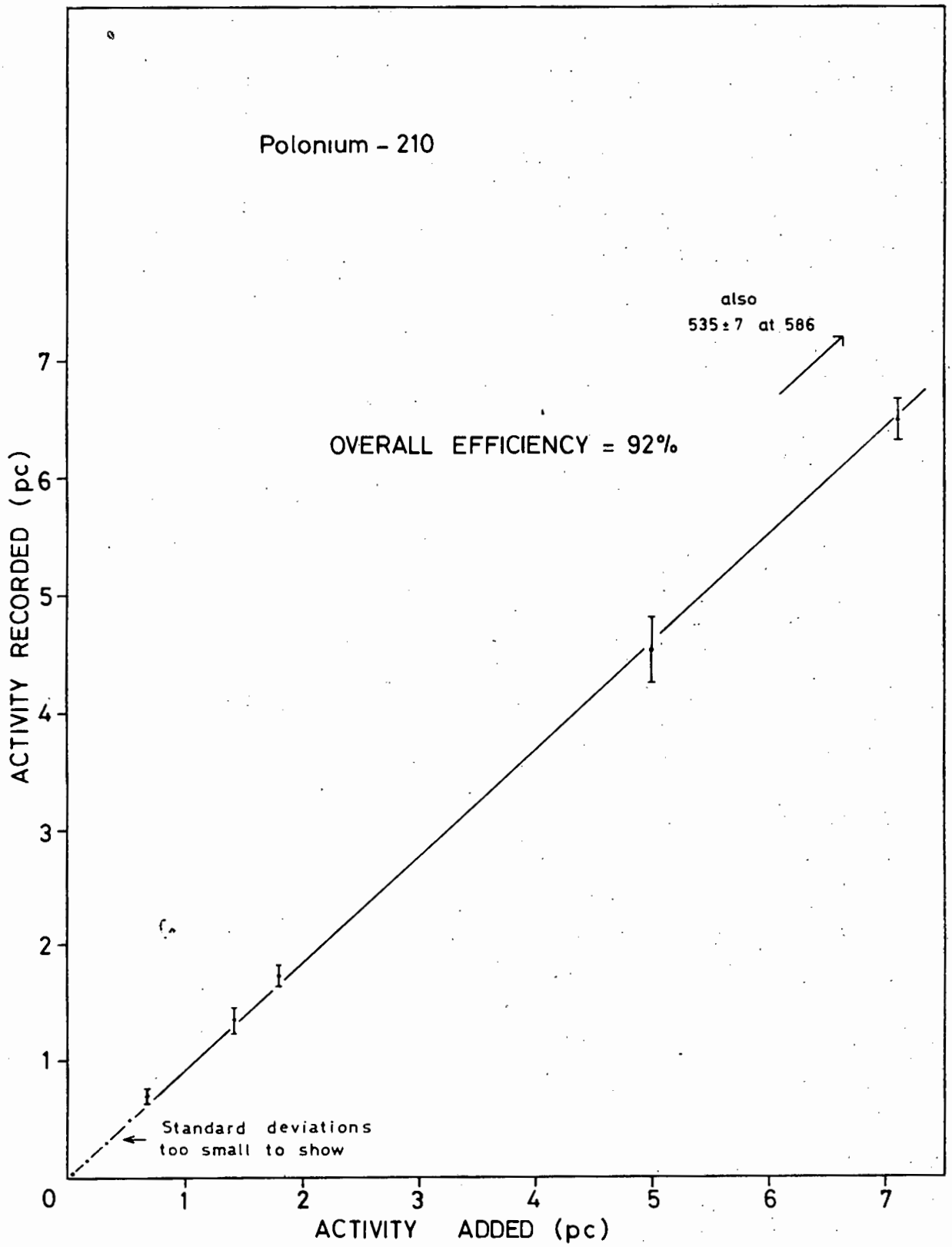

FIG. 14 CALIBRATION CURVE – POLONIUM · 210

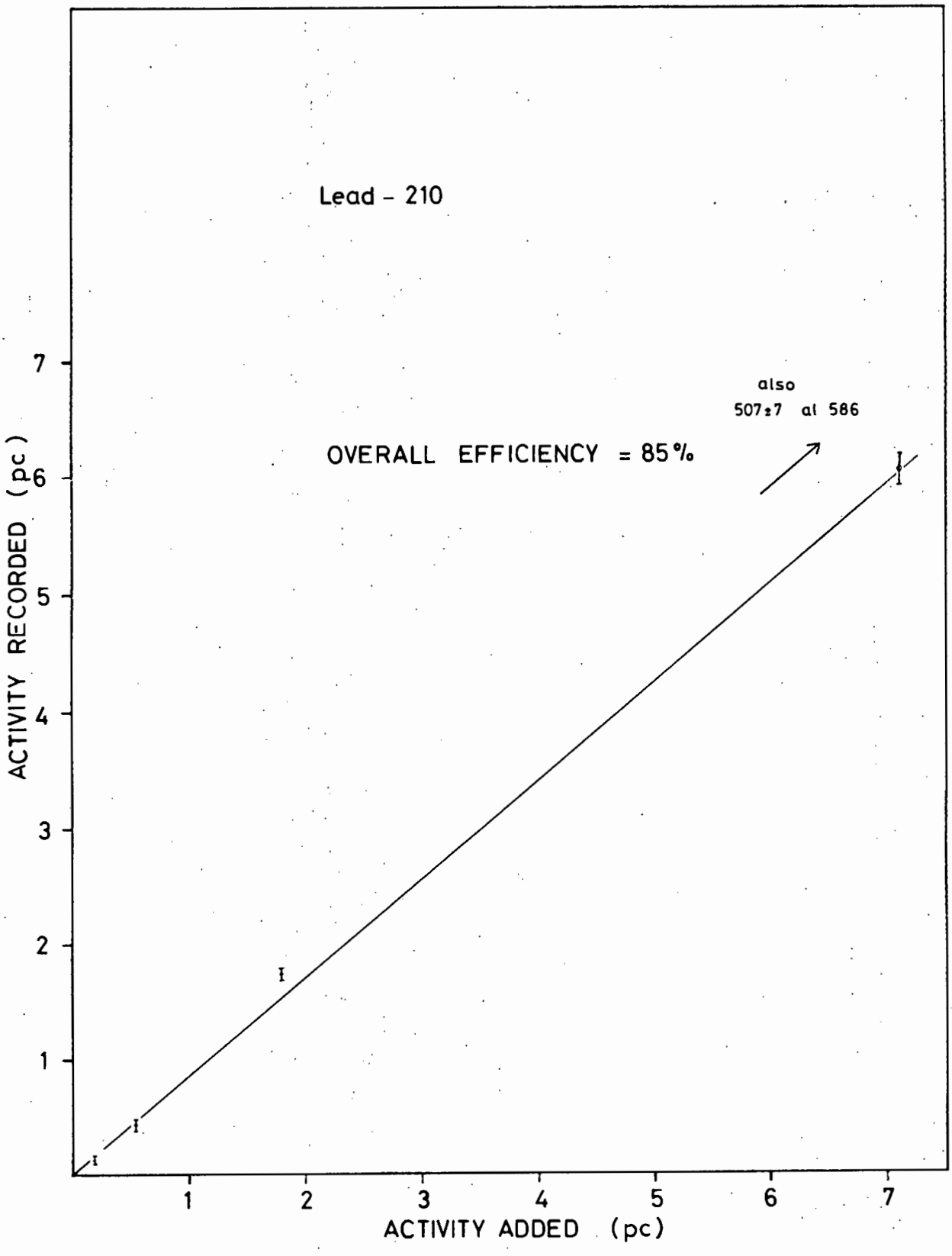

FIG.15 CALIBRATION CURVE — LEAD - 210

TABLE 8 Recovery of Polonium-210

Polonium-210 added to 1.5 l sea water (pc)	Polonium recovered after solv. extr. and plating (pc)
0.051	0.047 ± 0.003
0.156	0.168 ± 0.020
0.180	0.172 ± 0.013
0.34	0.29 ± 0.03
0.54	0.48 ± 0.02
0.68	0.70 ± 0.07
1.42	1.33 ± 0.13
1.80	1.74 ± 0.04
5.0	4.5 ± 0.3
7.1	6.5 ± 0.2
586	535 ± 7

APDC/MIBK system to extract metals of interest at the extreme dilutions present in the ocean may perhaps be of more general use.

All data presented have of course been corrected for unsupported polonium-210 decay and supported polonium-210 build-up and are expressed as activities at time of collection (see equations in Section 10.3.3). In the calculations the half-lives of lead-210 and polonium-210 have been taken as 21.4 years and 138 days resepctively.

4.1.3 Results[†]

Sea water samples were collected at a standard depth of 20 m at stations on separate cruises by R.S. Africana II and R.S. Sardinops during March 1969. This depth was chosen as representative of the upper mixed layer and at the same time free of possible contamination from the ship. The results of the polonium-210 and lead-210 measurements are given in Table 9. Activities have been expressed in units of 10^{-15} c/l (1×10^{-15} c/l is equivalent to 0.0022 d.p.m./l).

The stations occupied during cruise A (R.S. Sardinops) were situated along the West Coast close to Cape Town. Corresponding plankton samples were collected at these stations for biological removal estimates (see Section 4.2.1).

Cruise B (R.S. Africana II) covered a far wider area (this cruise in fact formed part of a combined survey of the Agulhas Current). The sea water samples for polonium and lead analysis were collected at 18 stations selected to provide a good coverage.

The horizontal distributions of polonium-210 and salinity at 20 m (cruise B only) are shown in Fig. 16. For purposes of comparison, the salinity distribution

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[†]Most of the findings in this section have already been published (SHANNON et al. 1970).

TABLE 9 Polonium-210 and Lead-210 in Sea Water at 20 m, March 1969

Station No.	Date	Latitude	Longitude	Polonium-210 (10^{-15} c/l)	Lead-210 (10^{-15} c/l)
Cruise A : R.S. Sardinops					
R/A 1	18/3/69	33°51'S	18°17'E	15 ± 2	30 ± 9
" 2	18/3/69	34°16'S	17°40'E	8 ± 2	17 ± 8
" 3	18/3/69	34°42'S	17°00'E	8 ± 2	<10
" 4	18/3/69	35°07'S	16°23'E	11 ± 2	31 ± 9
" 5	19/3/69	34°12'S	15°47'E	17 ± 2	35 ± 9
" 6	19/3/69	32°40'S	14°33'E	15 ± 5	16 ± 7
" 7	20/3/69	32°40'S	15°44'E	18 ± 2	17 ± 5
" 8	20/3/69	32°45'S	16°33'E	15 ± 2	<10
" 9	20/3/69	32°42'S	17°18'E	30 ± 5	15 ± 5
" 10	20/3/69	32°40'S	17°53'E	21 ± 2	<10
" 11	21/3/69	33°25'S	17°59'E	28 ± 2	<10

TABLE 9 continued:

Station No.	Date	Latitude	Longitude	Polonium-210 (10^{-15} c/l)	Lead-210 (10^{-15} c/l)
Cruise B : R.S. Africana II					
R/A 12	6/3/69	34°33'S	21°05'E	11 ± 2	32 ± 9
" 13	6/3/69	36°30'S	21°36'E	33 ± 2	37 ± 9
" 14	7/3/69	38°27'S	22°00'E	30 ± 3	55 ± 9
" 15	8/3/69	40°26'S	22°24'E	27 ± 2	51 ± 9
" 16	13/3/69	39°10'S	17°04'E	29 ± 3	38 ± 9
" 17	14/3/69	37°45'S	17°25'E	28 ± 3	19 ± 10
" 18	15/3/69	35°48'S	18°53'E	12 ± 2	24 ± 10
" 19	17/3/69	36°59'S	13°45'E	13 ± 2	84 ± 15
" 20	18/3/69	35°45'S	15°32'E	41 ± 4	<10
" 21	19/3/69	34°53'S	17°03'E	19 ± 2	37 ± 12
" 22	19/3/69	33°51'S	18°17'E	24 ± 2	91 ± 18
" 23	23/3/69	35°17'S	12°25'E	14 ± 2	74 ± 11
" 24	24/3/69	32°45'S	12°15'E	15 ± 2	135 ± 16
" 25	24/3/69	32°35'S	13°17'E	14 ± 2	98 ± 16
" 26	24/3/69	32°42'S	14°32'E	15 ± 2	11 ± 9
" 27	24/3/69	32°43'S	15°45'E	16 ± 2	47 ± 9
" 28	25/3/69	32°41'S	16°37'E	28 ± 3	68 ± 15
" 29	25/3/69	32°40'S	17°54'E	18 ± 2	15 ± 10

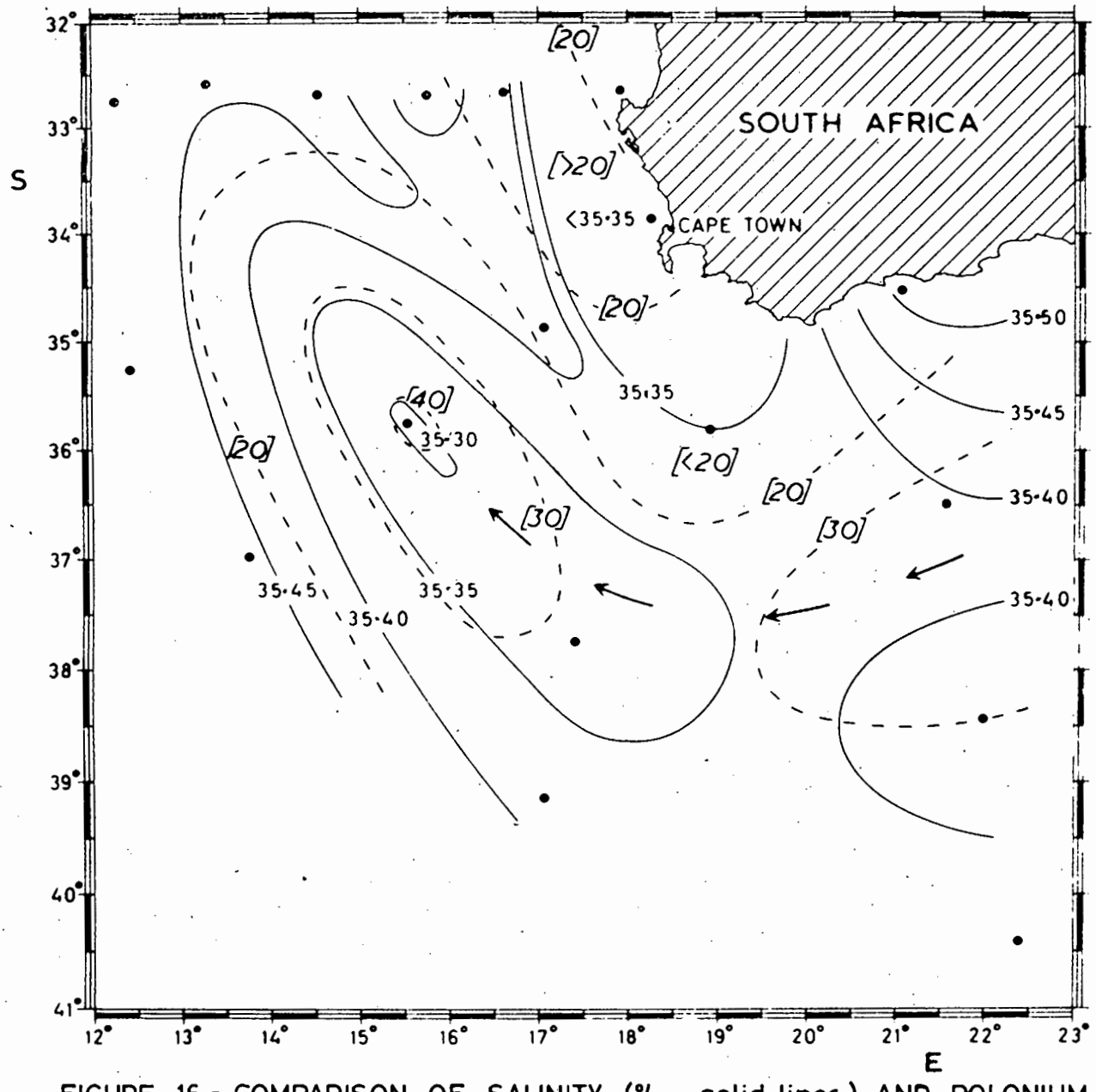

FIGURE 16 - COMPARISON OF SALINITY (‰—solid lines) AND POLONIUM-210 (10^{-15} c/l - VALUES IN BRACKETS, BROKEN LINES), CRUISE "B" MARCH 1969

in the figure has been drawn using data only from those stations at which polonium-210 measurements were made. The basic trend remains unaltered by the inclusion of the additional available values.

The polonium-210 content of the surface layer of the sea around the Cape of Good Hope during March 1969 varied between 8 × 10^{-15} c/l and 41 × 10^{-15} c/l with a mean value of 20 × 10^{-15} c/l or 0.044 d.p.m./l. During January and February, while the experimental technique was being tested, 4 samples were collected off rocky beaches around the Cape Peninsula. The data has not been included in Table 9 as it is considered that the proximity of rocks, sand and effluent outlets may have introduced contamination, but nevertheless the mean polonium-210 activity of these samples was 30 × 10^{-15} c/l. This figure is in good agreement with FOLSOM (1966) who obtained values of 30 × 10^{-15} and 37 × 10^{-15} c/l for samples collected off the Scripps Pier.

The lead-210 values presented in Table 9 are subject to large errors due to counting statistics. A conservative estimate of the effective lower detection limit of the method for lead-210 (using 1.5 litre samples and two month storage before counting) is about 10 × 10^{-15} c/l and results lower than this value have simply been tabulated as <10 × 10^{-15} c/l. The lead-210 activity of the surface layer during March 1969 ranged from "zero" (i.e.<10 × 10^{-15} c/l) to 135 × 10^{-15} c/l with a mean value of 38 × 10^{-15}c/l,

or 0.084 d.p.m./l. RAMA et al. (1961) obtained a value of about 0.11 d.p.m./l for the upper water layer in the Pacific, a figure in good agreement with these data.

It is evident from the data that there are considerable variations in the lead-210 and polonium-210 content. This is to be expected when the modes of influx and removal of these nuclides are considered.

A single depth profile at 32° 40'S, 14° 33'E comprising 4 samples at intervals between the surface and 600 m gave the following results (Table 10).

TABLE 10 Polonium-210 and lead-210 in a single depth profile at station R/A 6 (19/3/69) 32° 40'S, 14° 33'E

Depth (m)	Polonium-210 ($\times 10^{-15}$ c/l)	Lead-210 ($\times 10^{-15}$ c/l)
20	15 ± 5	16 ± 7
96	18 ± 3	21 ± 14
288	31 ± 3	35 ± 14
634	31 ± 3	22 ± 14

From the above table there does appear to be an indication of an increase in the polonium-210 content below 100 m. However the poor statistics of the lead-210 measurements preclude the drawing of positive conclusions. Further observations using larger samples will be necessary to establish the distribution of the lead/polonium-210 pair in deep waters. If the radium-226 content of the

water between 100 m and 600 m is taken as 4×10^{-14} g/l or 40×10^{-15} pc/l then it appears that both polonium-210 and lead-210 are not far off being in equilibrium with radium in South Atlantic Central Water (Central Water is discussed in Section 10.5).

The lead-210/polonium-210 activity ratio in sea water was about 2 on the average. Individual samples, however, showed an interesting trend. In most samples the activity ratio was greater than unity, but in about one third of the samples the ratio was near to, or less than one. Of these samples, 7 were collected in an area lying north-west of Cape Town (bounded by the coast and the 14^{o}E meridian) and two were from the eddy of Agulhas Water. (see Fig. 16). The possibility exists of using the lead-210/polonium-210 ratio for estimating the age of oceanic waters, but this can only be done when the complex processes involved are better understood.

Tracers were not used for the polonium-210 and lead-210 measurements, as it was not considered vital in a programme aimed primarily at determining the general levels of these nuclides in sea water. However now that interesting small variations are beginning to emerge the use thereof should be considered seriously. In addition larger water samples would be more representative. Without the use of tracers and large volume sampling, complete reliance cannot be placed on the validity of a single sample.

4.2 Marine Organisms

The unsupported polonium-210 content of some 400 samples of various marine organisms was determined by total alpha-counting by measuring the fall-off in activity with time. In addition, the total polonium-210 content (which of course includes supported as well as unsupported polonium-210), as determined by chemical extraction, involving wet ashing and plating onto silver, was performed on 17 plankton samples collected during March 1969 and six samples of pelagic fish caught during 1969. This extraction was carried out in order to evaluate both the polonium-210 and lead-210 levels in plankton and fish for bio-geochemical balance calculations, as well as to verify the results of total alpha-counting.

Under the general heading of Marine Organisms it is proposed to discuss the chemical extraction in the first instance and then secondly to discuss the unsupported polonium-210 measurements made on various organisms using the total counting technique.

4.2.1 Chemical Extraction

Plankton samples were collected at 11 stations on cruise A (see Section 4.1) and at stations 24-5 and 24-1.5. The samples were oven dried, finely ground and divided into two portions.

Half a gram of the first portion was transferred to a

150 ml glass beaker and wet-ashed in nitric and perchloric acids in a similar manner to BLACK (1961) and HOLTZMAN (1963). Briefly, the procedure is as follows:

Fifteen ml of 15.8 N A.R. nitric acid is added to the dried plankton, the beaker covered with a watch glass and left to stand for one hour. The beaker is then heated and the contents allowed to digest for an hour after which it is evaporated to dryness. After cooling, 20 ml of 70% A.R. perchloric acid is added, the beaker heated, and the contents allowed to digest for about an hour until no white fumes are evolved on the addition of a few drops of hydrochloric acid. The contents are then evaporated to dryness and subsequently dissolved in 10 ml of warm A.R. hydrochloric acid. The polonium-210 is plated out of the solution as described earlier. Immediately after the first plating a further plating is performed to both check the plating efficiency and to ensure that no polonium-210 remains in the solution. The plating efficiency was usually close to 100% and, in any event, better than 95%. As in the case of the sea water samples the plating solution was retained and again plated out after two months to determine the lead-210 contribution. As with the sea water samples all data presented have been corrected for unsupported polonium-210 decay and lead supported polonium-210 build-up, and are expressed as activities at time of collection. In the case of pelagic fish samples the extraction technique is identical except

that 1.0 g of dried sample is used.

The overall efficiency of the digestion and plating technique for polonium-210 and lead-210 was determined by a calibration run involving the addition of lead-210/ polonium-210 (in equilibrium) spikes ranging from 0.4 pc to 4.0 pc. In the case of polonium-210 the overall efficiency was 98% and for lead-210 it was 95%. As an additional check on the digestion and plating efficiency the second portion of each dried plankton sample was packed in a sealed sample phosphor system as previously described (Chapter 2: CHERRY, 1964; TURNER et al.1958a) and the alpha-activity of the resultant "thick" source determined by total counting. Subsequent recounting provided the unsupported polonium-210 contribution. Allowing for the lead supported polonium-210 contribution, the results were in good agreement with those determined by the digestion and plating technique (see Table 11). The loss of polonium during the extraction process (MARTIN and BLANCHARD, 1969) is considered to be negligible.

Attempts were made to establish a relationship between the activity of plankton per litre of sea water and the activity of the sea water, but no such trend was apparent. Plankton data have been tabulated in activity per wet weight of plankton rather than in activity per litre of sea water. In all cases the contribution of the netted plankton to the total polonium-210 activity of the sea water was less than 0.5%. The mean lead-210

TABLE 11 Comparison of unsupported polonium-210 values determined by two techniques

Sample Number	Unsupported polonium-210	
	Total alpha-counting pc/kg (wet)	Chemical extraction and electrodeposition pc/kg (wet)
Zooplankton		
180	116 ± 6	117 ± 4
181	340 ± 19	392 ± 7
182	218 ± 31	235 ± 5
183	380 ± 31	351 ± 4
184	373 ± 31	355 ± 11
185	485 ± 42	538 ± 12
186	647 ± 52	635 ± 13
187	460 ± 50	261 ± 12
188	507 ± 36	519 ± 10
189	455 ± 24	412 ± 8
190	285 ± 37	245 ± 7
191	192 ± 14	217 ± 6
192	181 ± 43	257 ± 7
Phytoplankton		
239	not detected	5 ± 1
240	91 ± 13	96 ± 5
241	32 ± 8	30 ± 2
242	sample spoiled	89 ± 5

The polonium-210 and lead-210 activites in plankton and pelagic fish are tabulated in Table 12.

TABLE 12 Polonium-210 and lead-210 in phytoplankton, zooplankton and pelagic fish

Sample No.	Station	Depth(m)	Polonium-210 pc/kg (wet)	Lead-210 pc/kg (wet)
Phytoplankton				
239	24-1.5	40-0	12 ± 1	7 ± 1
240	R/A 9	50-0	165 ± 3	69 ± 4
241	R/A 10	40-0	42 ± 2	12 ± 1
242	R/A 11	50-0	109 ± 4	20 ± 2
Zooplankton				
180	24-1.5	40-0	122 ± 4	5 ± 1
181	24-5	100-0	428 ± 7	36 ± 2
182	R/A 1	70-0	258 ± 6	23 ± 2
183	R/A 2	100-0	368 ± 4	17 ± 1
184	R/A 3	100-0	395 ± 11	40 ± 3
185	R/A 4	100-0	600 ± 11	62 ± 4
186	R/A 5	100-0	697 ± 13	62 ± 4
187	R/A 6	100-0	291 ± 12	30 ± 2
188	R/A 7	100-0	570 ± 10	51 ± 3
189	R/A 8	100-0	433 ± 8	21 ± 2
190	R/A 9	100-0	272 ± 7	27 ± 2
191	R/A 10	40-0	226 ± 6	9 ± 1
192	R/A 11	80-0	276 ± 7	19 ± 2
Pelagic fish				
285	See Appendix	surface	620 ± 30	8 ± 4
287	" "	surface	2030 ± 50	not detected
288	" "	surface	860 ± 30	not detected
289	" "	surface	1350 ± 30	not detected
291	" "	surface	1500 ± 30	21 ± 5
293	" "	surface	1180 ± 30	16 ± 4

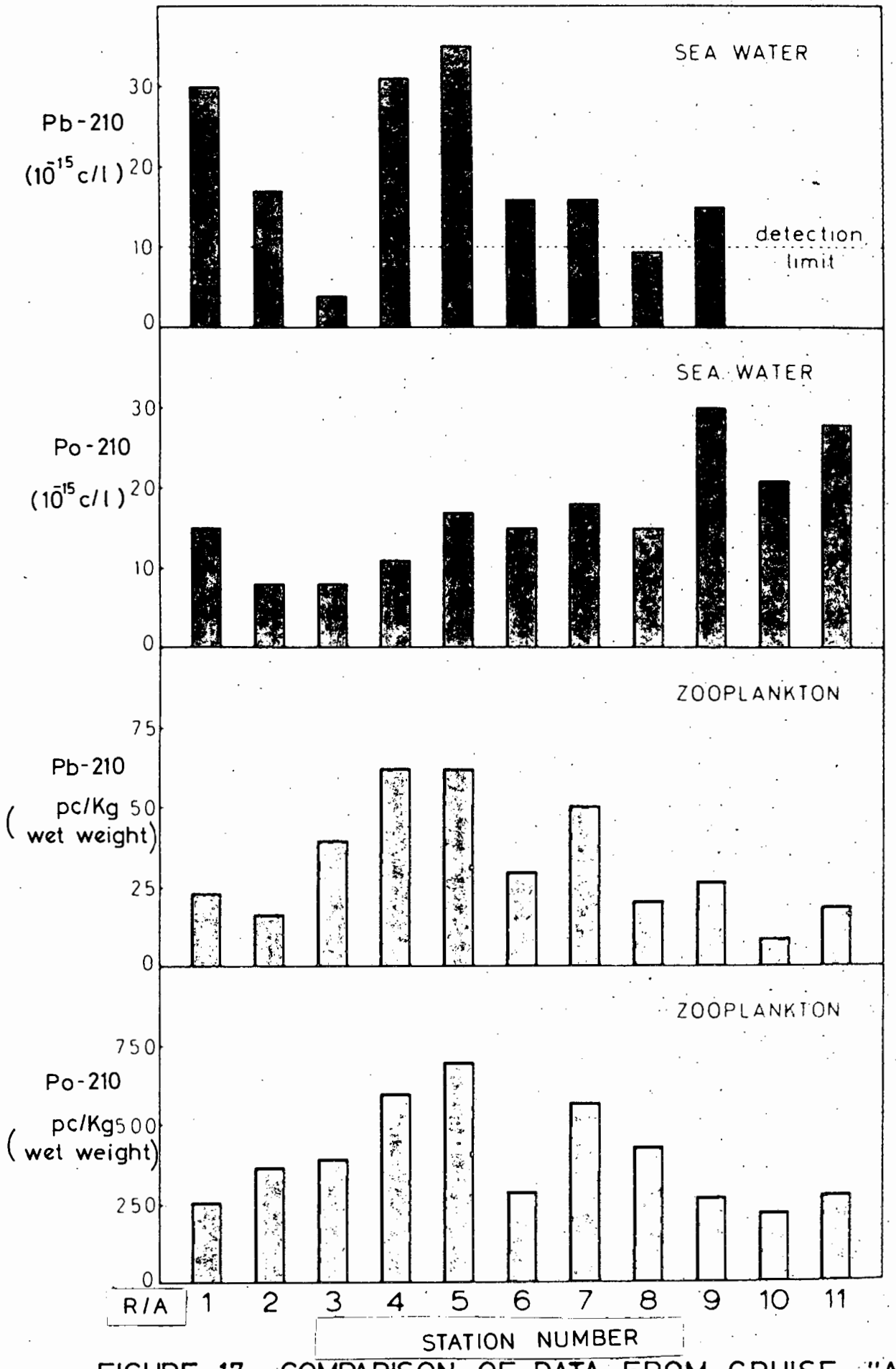

FIGURE 17 - COMPARISON OF DATA FROM CRUISE "A"

and polonium-210 activities of the zooplankton samples were 31 pc/kg (wet) and 380 pc/kg (wet) respectively. The variation of lead-210 and polonium-210 in plankton is best seen in Fig. 17, which is a graphical summary of corresponding polonium-210 and lead-210 data on sea water and plankton and illustrates certain features more clearly than the tables.

For the 13 zooplankton samples the average lead-210/polonium-210 activity ratio was 0.08 and the positive correlation co-efficient of 0.91 between lead-210 and polonium-210 was statistically highly significant (that is, greater than the 0.1% level). The corresponding atom ratio of lead-210/polonium-210 is about 5. For phytoplankton the lead-210/polonium-210 activity ratio appears to be in the range 0.2 - 0.5 with an atom ratio of about 18.

The average lead-210 content of both zooplankton and phytoplankton was similar, namely about 31 and 27 pc/kg wet material respectively. The polonium-210 content of zooplankton (380 pc/kg wet material) was however, a factor of about five higher than that in phytoplankton. This factor confirms earlier data (SHANNON and CHERRY, 1967; SHANNON, 1969) which showed that polonium-210 accounted for most of the alpha-activity in zooplankton and a smaller fraction in phytoplankton.

The mean polonium-210 and lead-210 concentrations in six samples of pelagic fish were 1260 pc/kg and

8 pc/kg wet material respectively, indicating a lead-210/polonium-210 activity ratio of 0.006 and an atom ratio of 0.4. It is difficult to compare these data with measurements made by BEASLEY (1968) and HOLTZMAN (1969) as these authors analysed various organs or components (e.g. soft tissue, hard tissue) of fish (mainly benthonic species). However, the lead-210 values are in approximate agreement with data given by these authors, although the polonium-210 values are higher. The above data indicate that the lead-210/polonium-210 ratio in pelagic fish is an order of magnitude lower than that in zooplankton, and it appears that the relative uptake of polonium-210 increases along the marine food chain.

From the data presented the enrichment (accumulation) factors of lead-210 and polonium-210 from sea water to wet zooplankton are about 815 and 19000 respectively. These results are in good agreement with earlier less accurate estimates (SHANNON and CHERRY, 1967). For phytoplankton the enrichment factors are about 710 for lead-210 and 4100 for polonium-210, and in pelagic fish the respective factors are 200 and 63000.

4.2.2 Unsupported polonium-210 as deduced from total alpha-counting

The alpha-spectra of zooplankton indicated that most of the alpha-activity in these organisms was due to alpha-unsupported polonium-210 (see Section 3.2). CHERRY (1964) and SHANNON and CHERRY (1967) observed that the

alpha-activity in most plankton samples showed a decrease with time compatible with the presence of a nuclide with a half-life of about 140 days - almost certainly polonium-210. In contrast these authors did not record any significant increases in activity with time, indicating that in general the bulk of the polonium-210 activity was due to an excess of polonium-210 over its effective parent lead-210. These findings were subsequently confirmed for plankton and extended to other marine organisms by BEASLEY (1968), HOLTZMAN (1969) and KAURANEN and MIETTINEN (1969).

Approximately 400 samples of marine life comprising numerous species collected over a wide area were analysed for excess polonium-210 by repeated total alpha-counting. A sample calculation is given in Section 10.3. All the results given in detail in Section 10.1 have been corrected for polonium-210 decay from time of collection and are expressed as at time of collection. The discussion that follows if of a general nature as specific variations and fluctuations in time and oceanographic locality are dealt with in Chapter 6.

The average concentrations of unsupported polonium-210 in various marine groups are given in Table 13, and conveniently summarised in Fig. 2 (see Section 2.3).

TABLE 13 Mean levels of excess (i.e. unsupported) polonium-210 in various marine organisms as deduced by total alpha-counting (errors are standard errors of the mean)

Organism	No. of Samples	Excess Po-210 Activity		Excess Po-210 Concentration	*Accumulation Factor
		pc/g(dry)	pc/Kg(wet)	10^{-18} g/g wet organism	
Zooplankton	211	9.4 ± 0.6	700 ± 40	160 ± 10	35 000
Agulhas phytoplankton	10	6.3 ± 2.5	280 ± 110	60 ± 24	14 000
Other phytoplankton	23	5.0 ± 1.3	290 ± 70	65 ± 17	14 500
Pelagic fish (whole)	13	4.5 ± 1.0	1200 ± 280	270 ± 65	60 000
Demersal fish (whole)	18	0.9 ± 0.2	260 ± 50	60 ± 11	13 000
Demersal fish (flesh)	7	0.4 ± 0.1	130 ± 40	30 ± 9	6 500
Demersal fish (liver)	4	4.3 ± 1.5	1100 ± 370	250 ± 85	55 000
Mollusc-soft tissue	15	4.4 ± 1.2	1300 ± 360	290 ± 80	65 000
Mollusc shell	15	0.3 ± 0.06	170 ± 35	40 ± 8	8 500
R/Lobster tail flesh	9	0.1 ± 0.05	20 ± 12	5 ± 3	1 000
R/Lobster shell	9	0.1 ± 0.05	60 ± 25	130 ± 55	3 000
R/Lobster digestive gland	9	32.1 ± 7.8	12600 ± 3100	2800 ± 680	630 000
Seaweed	13	0.4 ± 0.2	70 ± 35	16 ± 8	3 500

*Considering the polonium-210 content of sea water as 4.5×10^{-18} g/l (20×10^{-15} c/l).

Activities are expressed both on a fresh (wet) and a dry basis. Owing to the uncertainty in the concentration factor from wet plankton to dry plankton the in vivo activities for plankton should be regarded as conservative. The accumulation factors in Table 13 are for unsupported polonium-210 only. Thus the true accumulation factors will be higher.

The mean levels of unsupported polonium-210 in zooplankton and phytoplankton are about a factor two higher than the values reported earlier by SNANNON and CHERRY (1967). This discrepancy is largely due to sampling locality - most of Shannon and Cherry's samples were collected in the coastal waters associated with the Benguela Current while the data presented here is based on plankton collected over a wide oceanographic area. BEASLEY (1968) recorded a value of 0.55 d.p.m./g (.24 pc/g) wet weight for the polonium-210 content of mixed plankton samples - viz. a similar order of magnitude to the excess polonium-210 concentration in copepods from the Benguela Current. The level of excess polonium-210 in phytoplankton from the Agulhas Current (280 pc/Kg wet material) is similar to that observed in phytoplankton from other regions.

The activity of whole pelagic fish due to excess polonium-210 was typically 1200 pc/Kg wet material, a value higher than that observed in phytoplankton and zooplankton. The common pelagic fish found in the

Benguela Current (pilchard, anchovy, mackerel, red-eye sardine) are filter feeders, with phytoplankton and zooplankton in varying proportions comprising their diet (DAVIES 1957). No attempts have been made to determine in which organs of these fish the bulk of the polonium activity is distributed owing to difficulties associated with dissection and availability of fresh samples (most of the commercial catch is used for fishmeal production). However it is more realistic to compare whole pelagic fish with zooplankton and phytoplankton. The mean unsupported polonium-210 contents of phytoplankton and zooplankton from the Benguela Current (see Chapter 6) were 120 and 300 pc/Kg wet material respectively. Thus the available data strongly suggest that the concentration of unsupported polonium-210 increases along the food chain in the sequence: sea water - phytoplankton - zooplankton - pelagic fish. The implications of the use of fishmeal (manufactured from pelagic fish) as a source of protein for human consumption have already been discussed, and it would be logical to follow up this research with similar analyses on the pelagic fish predators (game fish such as tuna, sea birds such as cormorants and gannets). To date only two samples of tuna flesh have been analysed and in these excess polonium-210 was not detected.

Demersal fish are non filter feeders, feeding instead on benthic and midwater organisms. The unsupported polonium-210 content of whole demersal fish was relatively

low - only about one fifth of the pelagic filter feeders. The flesh of the demersal fish has an activity due to excess polonium-210 lower than that of the whole fish while most of the polonium seems to be concentrated in the liver (refer to Table 13). The preferential uptake of polonium-210 by the livers of terrestrial mammals has been noted by various workers (HILL 1965; BEASLEY and PALMER, 1966; CHERRY et al. (in press). Cherry et al. give the levels of excess polonium-210 in the livers of creatures from marine and terrestrial domains. They found that marine livers contained an order of magnitude higher alpha-activities (mostly unsupported polonium-210) than those observed in the livers of animals such as cattle, sheep and pigs and in the liver of man.

The marine molluscs collected for the survey of alpha-activity are predominantly filter feeders and the soft tissue (flesh and entrails) of these organisms displays a relatively high level of unsupported polonium-210, viz. about 1300 pc/Kg wet material. The shells of the molluscs on the other hand have a corresponding activity of about 170 pc/Kg wet shell. The activity of the whole mollusc will be intermediate between the activities of the tissue and shell. Abalone (perlemoen) are non filter-feeding molluscs, grazing instead on seaweeds, and the three samples analysed displayed a mean excess polonium-210 content of less than 200 pc/Kg wet tissue, or about one seventh the mean for all the molluscs. Single samples

of a whelk and a periwinkle also indicated a lower than average activity.

Molluscs, in particular the black mussel Aulacomya magelanica comprise much of the food of rock-lobsters, while the remainder of their diet is composed of echinoids, other rock-lobsters, crabs and seaweeds (HEYDORN, 1969). In view of this it is little surprising that the digestive gland of the rock-lobster contains a comparatively high level of unsupported polonium-210. In the initial stages of this research, samples of rocklobster were analysed as whole lobster, as flesh and as shell. As the whole rock-lobster (sample 294) had a significantly higher alpha-activity (1470 pc/Kg wet material) than the shell (500 pc/Kg wet shell) and the flesh (175 pc/Kg wet flesh), disections were performed on further samples (nos.302-309) to establish in which organ the activity was concentrated. It was found that nearly all the alpha-activity was contained in the digestive gland (an organ corresponding closely to the liver in other animals) and that most of this activity was due to unsupported polonium-210. The mean level of unsupported polonium-210 in this gland was 12600 pc/Kg wet material, a value considerably higher than those reported in the livers of caribou by BEASLEY and PALMER (1966) and reindeer by HILL (1965). The highest polonium-210 concentration was measured in sample 309, (34000 pc/Kg wet material) which was the digestive organ of a rock-lobster caught near Robben Island during April

1968. This is probably one of the highest natural activities recorded in any biological material. Few measurements have been made on the concentration of unsupported polonium-210 in whole rock-lobster but it does seem that the level of this nuclide increases down the food chain in the sequence: sea water - plankton - mollusc - rock-lobster.

By considering a polonium-210 concentration in sea water of 20 pc/l (4.5×10^{-18} g/l) the approximate accumulation or enrichment factors for the uptake of unsupported levels of this nuclide by various marine groups have been calculated and are given in Table 13. The enrichment factors in zooplankton and phytoplankton are about 35000 and 14000 respectively - viz. approximately twice as great as the enrichment factors given in Section 4.2.1. This discrepancy is due to the fact that many oceanic plankton samples with activities higher than the coastal samples have been included in the calculation of the mean values. The polonium-210 content of 20 pc/l is applicable to waters within a 500 km radius of Cape Town and it is possible that true oceanic water may contain more polonium-210. Oceanic water generally has a much lower plankton content than inshore water around South Africa and, if biological removal is an important mechanism whereby polonium-210 is removed from the surface layer, then it is probable that in the offshore water polonium-210 is more nearly in equilibrium with

its parent. By considering zooplankton and phytoplankton from the Benguela Current only, the accumulation factors are 15000 and 6000 respectively.

Polonium-210 is concentrated to a high degree in pelagic fish, in the soft tissue of molluscs and of course in the digestive glands of rock-lobsters. Lower accumulation factors are found in the flesh of fish and rock-lobsters, in seaweed and in the shells of molluscs and rock-lobsters.

With the exception of phytoplankton the activity due to excess polonium-210 in marine organisms expressed in pc/Kg wet material can be approximately equated to the radiation dose received in millirem/yr (R.B.E. = 10). - refer to Table 13. The implications of the dosimetry have already been considered in some detail in the Section 2.3. The results indicate that unsupported polonium-210 is responsible for most of the internal radiation dose received by marine organisms. In comparison the radiation doses due to the natural beta emitters and external sources are small in most marine groups. BEASLEY et al. (1969) consider that, should marine concentrates be used on a large scale as protein substitutes for human consumption, then the lead/polonium-210 pair could conceivably become the principal source of man's skeletal radiation dose. However, as unsupported polonium-210 accounts for much of the alpha-activity in many marine groups (pelagic fish in particular) and as

this nuclide has a half-life of only 138 days, storage of marine concentrates for a period of nine months would effectively reduce the concentration of polonium-210 to one quarter of its original level.

The problem that remains to be solved is to the reason why marine creatures preferentially assumulate polonium-210 over lead-210. BEASLEY (1968) considers that this may be due to the effective half-lives which these nuclides display in the organisms residing in the ocean. Beasley states, "If the effective half-life of lead-210 in marine species is long compared to that for polonium-210, the approach to equilibrium would be slower, and hence at times far from equilibrium, polonium-210 would be present in higher concentrations than would lead-210". Beasley considers that the age of the organism might be important in correlating lead-210 concentrations with those of polonium-210, and for this reason he does not quote accumulation factors for these nuclides. However, the data presented in the previous section indicate that the lead-210/polonium-210 ratio decreases in the sequence: phytoplankton - zooplankton - pelagic fish, which is also the sequence in which the life expectancy of the organism increases. In addition, the examination of a cross-section of five size (age) groups of rock-lobsters collected at the same locality during October 1968 showed no significant increase in the unsupported polonium-210 content of the digestive gland (see Table 14).

TABLE 14 Excess Polonium-210 in the Digestive Gland of Five Size Groups of Rock-lobsters

Sample No.	Carapace Length (mm)	Excess Po-210 in Digestive Gland (pc/Kg wet material)
336	59.9	5020 ± 436
337	63.5	14150 ± 1480
338	77.0	8070 ± 900
339	89.6 (approx. legal size limit)	8380 ± 1670
340	111.6	5320 ± 1180

Studies on the direct uptake of polonium by plankton from sea water were not feasible in the laboratory. However twelve samples of live fish of the same species (Acantholatris monodactylus) and approximately the same size were exposed to an artificially high lead/polonium-210 activity of 20 pc/l in a closed system sea water aquarium tank and fed on a standard diet. No significant increase in the polonium content of the whole fish was observed over a period of 18 days. The closure of the Sea Point Aquarium soon afterwards precluded further experiments.

Although polonium-210 accounts for a large part of the alpha-activity, its absolute concentration on a w/w basis is very small - in fact only about 10^{-13} g/Kg wet material. The preferential uptake of polonium-210 may

be associated with the chemistry of polonium. The common oxidation states of polonium are +2 and +4 and polonium reacts with a number of metals to form polonides, and a number of basic salts are known (TAYLOR, 1970). Taylor states that an important property of polonium compounds is their tendency to hydrolyse in aqueous solutions to form polymeric or colloidal species and he considers that polonium protein complexes may well be present in most foodstuffs. In sea water it follows that polonium may be associated with the carbon or be present to some extent in a colloidal state (43% of the radio isotopes of tellurium, the congenor of polonium in the periodic table, are present in colloidal form in sea water - POLIKARPOV 1966).

The uptake of polonium-210 by marine organisms may however be secondary. It is known that polonium has an affinity with certain metals such as copper, nickel, silver, gold and platinum at a low pH. (TAYLOR 1970), and use is made of this property in the assay of polonium by electrodeposition. It is also known that some transition elements, in particular iron, manganese and copper play an important role biologically. Data extracted from VINOGRADOV (1953) and GOLDBERG (1963) indicate that silver is accumulated by marine life by a factor of 10^4 to 10^5 , while stable lead is concentrated by a factor of 10 less. These factors are remarkably similar in magnitude to the accumulation factors of

polonium-210 and lead-210 in plankton and it is consequently considered possible that, in sea water, polonium may be associated with the trace element silver. This should however be regarded as speculative, but nevertheless it does seem to be a possibility, especially in view of the fact that silver is enriched in the livers of marine molluscs (VINOGRADOV, 1953) and also as fall-out silver-110 has been detected in the spiny lobster (SEYMOUR, 1963).

Another explanation may be the possible association of polonium with copper. Data given by NICHOLLS et al. (1959) indicates that plankton accumulate copper by a factor of about 25000 and lead to a lesser degree viz. by about 3000 times. Again these figures are compatible with the polonium-210 and lead-210 data.

4.3 Bio-geochemical Balance in the Sea

The following discussion is primarily based on the measurements made on polonium-210 and lead-210 in plankton and sea water during March 1969, and reported in Sections 4.1 and 4.2.1.

In order to calculate the removal times for polonium-210 and lead-210 it is necessary to have a quantitative estimate of the rate of influx of these nuclides into the sea. RAMA et al. (1961) quote the input into the atmosphere of radon-222 as 42 atoms per minute per square

centimeter of land. This implies that the average standing crop of radon in the atmosphere is 42 disintegrations per minute per square centimeter of land area. In another calculation LAMBERT et al. (1966) estimated that 2.5×10^{25} radon atoms are emanated annually by the continents. Excluding Antarctica this yield corresponds to 35 atoms per minute per square centimeter of land area. The agreement with the radon value of Rama et al. is reasonable. The land area of the southern hemisphere (excluding Antarctica which is covered by a layer of ice) is about 13.5% of the total hemispherical area (SVERDRUP, et al. 1942). Assuming no hemispherical interchange of atmosphere on the short time scale involved, assuming equilibrium between radon emanated and lead-210 deposited (LAMBERT et al. 1966) and assuming equal deposition of lead-210 over land and oceanic areas, then these values imply that on the average something like 5 atoms of lead are deposited per minute per square centimeter of total area in the southern hemisphere, i.e. about one third of the value for the northern hemisphere. This estimate should be considered as a maximum for deposition over oceanic areas because the short time scale will presumably imply a preferential deposition over land rather than oceanic areas.

Data extracted from PIERSON et al. (1966) indicates that during the period 1961-1964 the average lead-210 contents of coastal rain in the northern and southern

hemispheres (excluding Ottawa and Melbourne which are considered as being continental) were 2.46 pc/l and 0.88 pc/l respectively. Thus on the average the southern hemispherical oceanic areas have a lead-210 content in rain which is about 36% of that of the northern hemisphere, i.e. a figure in fair agreement with the effective distribution of land in the two hemispheres. Very little data on true oceanic rainfall is available. Figures cited by LOEWE (1957) indicate a rainfall over the sea between latitudes 45°S and 70°S of about 80 cm per year. BLIFFORD et al. (1952) quote the total rainfall over land as 99×10^3 km^3/year, which implies an average rainfall over land of 67 cm/year. If we assume that the average rainfall over the sea in the southern hemisphere is 70 cm/year and assume further that this rainfall contains 0.88 pc/l of lead-210, then each square centimeter of area received 0.062 pc of lead-210 per year or 4.2 atoms per minute. This figure is to be compared with the "maximum" fall-out estimate of about 5 atoms per minute per square centimeter calculated above from the consideration of land areas and production rates of radon-222. It is perhaps a little surprising that these values are in such close agreement.

It will therefore not be unreasonable if a southern hemisphere atmospheric fall-out rate of lead-210 of 5 atoms per minute per square centimeter is used. Suppose a very simple two layer ocean with the atmospherically produced

lead-210 fall-out distributed throughout the upper 100 m is considered. Let us assume that there is no interchange between deeper waters and the surface layer. The input of lead-210 into this layer from the atmosphere is therefore 0.5 atoms per minute per litre. Let us also assume that no vertical mixing takes place. Thus the following balance equation may be set up:

$$\frac{dN}{dt} = 0 = I - \lambda N - RN$$

where N is the concentration of lead-210 in the mixed layer, I is the total input rate of lead-210 into the mixed layer from both atmospheric lead-210 fall-out and decay of radium-226 in sea water, λ is the radioactive decay constant for lead-210, and R is the probability per unit time of a lead-210 atom being removed by biological and inorganic removal processes. R is called the "rate constant" while the reciprocal of R is customarily referred to as the "removal time" for the isotope concerned.

Two recent papers (BROECKER et al. 1967; SZABO, 1967) have given the radium-226 content of the surface water of the Atlantic and Pacific Oceans as $4\text{-}5 \times 10^{-14}$ g/l. Broecker et al. have however shown that radon-222 is not in equilibrium with its parent in the surface layer, the radon-222/radium-226 activity ratio for the upper 100 m being between 0.4 and 0.8. For the purpose of the calculation it is proposed to consider that the radon-222 concentration in the surface layer is equivalent to

3×10^{-14} g/l of radium-226. This implies a production rate of lead-210 of 0.067 atoms per minute per litre, giving the total input I = 0.5 + 0.067 = 0.57 atoms of lead-210 per minute per litre.

Inserting this value and the measured mean lead-210 content of 0.0084 d.p.m./l into the balance equation gives $R = 0.19$ years^{-1} . The implied removal time for lead-210 is therefore about 5 years. RAMA et al. (1961) found a removal time for lead-210 of 2 years for the North Pacific Ocean. The difference between their estimate and this is due largely to the fact that they used the lead-210 fall-out rate applicable in the Northern Hemisphere, viz. 15 instead of 5 atoms per square centimeter per minute.

A similar balance equation can be set up for polonium-210. From rainfall data it appears that in rain the polonium-210/lead-210 activity ratio varies from about 0.1 to 0.3. The precise ratio is not very important as these values correspond to an input from the atmosphere of about 0.001 to 0.003 atoms of polonium-210 per minute per litre in the mixed layer (i.e. small amounts). The input from lead-210 decay (based on the data presented) is 0.084 atoms per minute per litre while the polonium content of the mixed layer was found to be 0.044 d.p.m./l. Inserting these values in the balance equation it is found that $R = 1.8$ years^{-1} i.e. a removal time for polonium-210 of 0.6 year. If we take into account the supply of polonium-210 and lead-210 from deeper waters then

the removal times for both these nuclides will be shorter. The rate of upwelling along the West Coast can be as much as 20 m per day (VISSER, personal communication) and this could conceivably give rise to a net supply of lead-210 into the surface layer from deeper water of 50 atoms per minute per square cm. However as upwelling is not continuous and is confined to the inshore region of the West Coast its overall contribution to the input of lead-210 in the whole area under discussion is difficult to establish. Many more observations will be required to establish the contribution from deeper waters.

In the case of radium-226 the removal times could not be calculated in a similar manner to those for lead-210 and polonium-210 owing to lack of input data. However, for comparison with the removal rates computed above, the removal times for lead-210 and polonium-210 were, in addition, calculated by following a similar argument to the one given for radium-226 in Chapter 3. By considering the rate of removal of organic matter (dry) from the upper 100 m layer as 6×10^{-2} g/cm^2/yr (see Section 3.3) and assuming that the polonium-210 and lead-210 contents of this dry material are similar to those of phytoplankton, viz. about 5 pc/g and 1.7 pc/g respectively, i.e. taking the polonium-210 value from Table 13 and assuming that lead-210 constitutes $\frac{1}{3}$ of this value), and also that the polonium-210 and lead-210 contents of the surface layer are 20×10^{-15} and 38×10^{-15} c/l respectively, then

the respective removal times for these nuclides are 0.7 and 4 years. These results, which are calculated by making crude assumptions about biological activity, are surprisingly similar to the removal times calculated earlier using more relaibale input data. Accordingly it does seem that the assumptions about biological activity as set out in Section 3.3 are at least reasonable.

It is interesting to note how the atom ratio of lead-210 to polonium-210 decreases steadily from the fall-out rainwater to the pelagic fish. In air this ratio is 581, in rain water about 400, in seawater 111, in phytoplankton 18, in zooplankton 5 and in pelagic fish 0.4. It is furthermore perhaps significant that the data plus the rate factors calculated above imply that the ratio of lead-210 to polonium-210 atoms removed per unit time from the sea water in the upper mixed layer in order to maintain balance is about 12. The similarity of this figure to the corresponding atom ratio in plankton might be an indication that biological removal by plankton is the prime removal mechanism for both ponolium-210 and lead-210.

It is more likely that removal is due to phytoplankton than zooplankton, as the biomass of the mixed layer as determined by hauls of standard zooplankton nets on Cruise A was only 1.5×10^{-4} g wet plankton per litre of sea water. Even though net data in unreliable as an estimate of biomass, it is nevertheless difficult to ascribe removal to zooplankton from consideration of the

above value. If the polonium-210 content of zooplankton is taken as 400 pc/kg wet weight then, in order to maintain the removal of polonium-210 from the sea water indicated by these data, the plankton would have to be replaced approximately every 16 hours. However, it is possible that the removal of polonium-210 and lead-210 from the sea water may be associated with diurnal migrations of zooplankton. VINOGRADOV (1961) postulated a cellular scheme of migrations of zooplankton. He considers that the most important way of supplying food to the deep ocean is by active transport of organic matter from the upper zone by migrating animals. At night a great number of interzonal animals ascend to the surface to feed on phytoplankton and minute animals, descending at day to depths of some hundred metres. Thus organic matter produced at the surface is actively carried to the deep ocean along a "ladder of migrations". His hypothesis is largely based on the fact that apart from deep-bottom animals, the main mass of the deep sea pelagic animals are carnivorous and not detritus eaters. Such a cellular scheme could indeed be responsible for a relatively rapid system of removal of lead-210 and polonium-210 from the surface layer, but must be regarded as speculative until such time as more detailed experimental data are available.

5. THORIUM MEASUREMENTS

The discovery of a marked disequilibrium between thorium-232 and thorium-228 in sea water by MOORE and SACKETT (1964) generated considerable interest in the thorium series elements and raised intriguing problems, with the result that several papers relating to thorium in the sea have appeared during the last few years. The present state of knowledge has been discussed in some detail in Chapter 1.

Little is known about thorium in marine life. As stated in Chapter 1, CHERRY (1964) and SHANNON (1969) indicated that thorium series activity was present in marine plankton at a level of about 1 pc/g dry material, while recently CHERRY et al. (1969) gave results of thorium-228 measurements in plankton and sea water.

The plankton data embodied in CHERRY et al. (1969) together with additional material from total "alpha-pairs" counting has been supplemented by measurements of the thorium isotopic ratios in plankton, and is considered in this chapter.

5.1 Thorium-Isotope Ratios in Plankton

Before any positive conclusions could be drawn from the "alpha-pairs" data, it was necessary to establish the degree of equilibrium between the thorium series elements.

The chemical extraction procedure employed was similar to the method of KU (1966). This technique involves chemical extraction of thorium by ion exchange and solvent extraction followed by the preparation of a thin source and alpha-spectrometric analysis. Details of the technique are summarised as follows.

5.1.1 Thorium Extraction Technique

(a) Anion exchange column: A 12 cm × 1 cm column packed with Dowex AG 1 × 8 (100-200 mesh) anion exchange resin was used. The resin was pre-treated by washing with 40 ml double glass-distilled water followed by 40 ml of 8N hydrochloric acid.

(b) Cation exchange column: An 8 cm × 1 cm column packed with Dowex 50 W × 16 cation exchange resin was used. The resin was pre-treated by washing with 40 ml double glass-distilled water followed by 40 ml of 4N hydrochloric acid.

(c) Outline of procedure: Approximately 0.5 g oven dried plankton was wet ashed in nitric and perchloric acids as described in Chapter 4. The residue was subsequently dissolved in concentrated hydrochloric acid and the solution stored in a clean polythene bottle. Immediately prior to analysis the solution was adjusted to 8 N by the addition of double glass-distilled water. The sample solution was then passed through the pre-treated anion exchange column and the column washed with 50 ml 8 N hydrochloric acid.

The effluent was adjusted to 4 N by the further addition of double glass-distilled water, and this solution was then passed through the cation exchange column. (During the anion sorption phase uranium and iron are adsorbed onto the anion resin and are eluted from the same by addition of 50 ml of 0.1 N hydrochloric acid - KU, 1966). The cation exchange column was washed with 30 ml 4 N hydrochloric acid, and the effluent discarded. (During the cation sorption phase thorium and protoactinium are adsorbed onto the cation resin - KU 1966). The thorium was eluted into a 150 ml glass beaker by passing 40 ml 0.75 M oxalic acid solution through the column. To prevent possible adsorption of thorium onto the glass 200 μg lanthanum chloride was added to the eluate. The eluate was decomposed by fuming with a nitric acid (5 ml)/ perchloric acid (5 ml) mixture. After fuming was complete the walls of the beaker were washed with perchloric acid, a second fuming carried out, and the contents of the beaker taken to dryness. The residue was subsequently dissolved in 8 ml of 0.1 N nitric acid and transferred to a 50 ml separating funnel.

Two ml of 10% w/v 2-thenoyl-trifluoroacetone (TTA) in benzene were added and the contents of the funnel shaken vigorously for 45 minutes. The funnel was allowed to stand for 10 minutes after which the aqueous portion was run off and discarded. The solvent layer was evaporated onto a stainless steel planchet and the organic residue

was effectively removed by baking the planchet in an electric furnace at 700°C for 3 minutes. The resulting thin source was counted for typically 50-100 hours on a semiconductor alpha-spectrometer of the type described in Chapter 10. Reagent/background blanks were prepared in a similar manner. The positions of the thorium peaks in the spectrum were checked by counting a known thorium source. Results were corrected for the reagent/background contribution.

As the primary purpose of the above was to estimate the activity ratios between the thorium isotopes in plankton and not the absolute activities, thorium spikes were not used to measure the efficiency. However repeated total "alpha-pairs" counting prior to chemical extraction provided a good estimate of the absolute activities and these data were accordingly used to calibrate the activity contributions of the individual thorium isotopes in plankton. The overall extraction and counting efficiency was about 20%. In the calculations the width of each spectral peak was taken as 280 KeV (6 channels) which corresponds to twice the width at half height of the average thorium-228 peak. The errors quoted for the individual activities are standard deviations due to counting statistics.

Except for the TTA and lanthanum chloride (both BDH), "Analar" reagents were used.

5.1.2 Results and Discussion

The prime purpose of the thorium spectra measurements was to establish the degree of equilibrium between the thorium isotopes -228 and -232 in plankton in order that the "alpha-pairs" data could be interpreted.

In sea water the thorium-228/-232 activity ratio is about 15 (MOORE and SACKETT, 1964; SOMAYAJULA and GOLDBERG, 1966). If thorium itself is preferentially accumulated by plankton and other marine organisms it might be expected that a similar activity ratio will be found in marine life. However, if marine organisms accumulate radium-228 in addition to thorium, then the thorium-228 concentration may be further enriched by the decay of radium-228.

All the thorium-spectra showed conclusively that thorium-228 and daughters accounted for most of the thorium series alpha-activity in plankton. The spectra did show small peaks in the thorium-232 and thorium-230 positions and even though the resolution and statistics associated with these isotopes was poor, it was possible to draw some conclusions. An example of the thorium spectrum of a phytoplankton sample (No. 220) is shown in Fig. 18. The resolution and statistics in the thorium-230 and -232 peaks in this case was somewhat better than in most other samples but the characterisation of the thorium-228 and daughter peaks was typical.

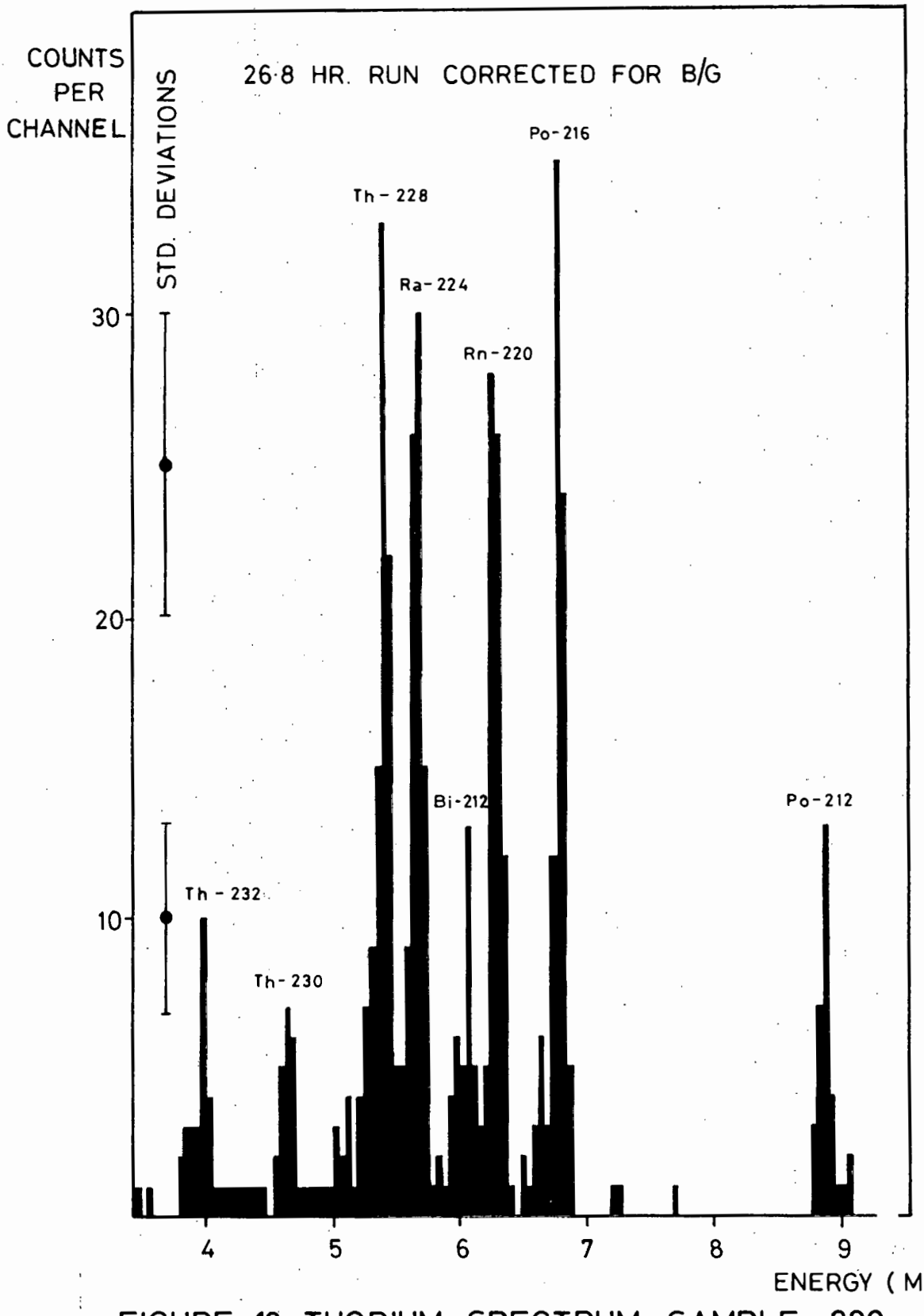

FIGURE 18 THORIUM SPECTRUM - SAMPLE 220

With the knowledge that thorium-228 is the effective head (alpha) member of the thorium series in plankton, the activity concentration of the nuclide can be calculated to a good approximation by multiplying the thorium series activity as deduced from the alpha-pairs technique by one fifth. The error associated with this approximation will be not more than about 5% in most instances.

The results of the measurements of thorium-228, -230 and -232 in eight zooplankton and seven phytoplankton samples are given in Table 15. The thorium-228 activities have been taken as one fifth of the thorium series activity as deduced from the alpha-pairs technique and the thorium-230 and -232 activities from the semi-conductor data have been "calibrated" accordingly. This to some extent accounts for the relatively large standard deviations in the thorium-230 and -232 results. The standard deviations of the activity ratios have however been calculated directly from the semi-conductor data.

Although the plankton samples were analysed for thorium series activity by total alpha-pairs counting soon after collection, the chemical extraction for thorium spectra analysis was not carried out immediately, but at an interval of 12-27 months after the plankton was caught. The main difficulty with the interpretation of the results is that without radium-228 measurements it was not possible to establish with certainty to what extent thorium-228 was supported by radium-228. MOORE and

SACKETT (1964) and MOORE (1969a,b) made use of the levels of thorium-228 that had "grown in" in shells to estimate the level of radium-228 in coastal waters. This is based on the assumption that thorium-228 in shells is present due to a preferential uptake of radium-228, and not as a result of preferential accumulation of thorium-228 (if the latter were the case then the radium-228 concentrations in coastal waters would be significantly lower than those predicted by Moore). MOORE (1969b) also determined the radium-228/radium-226 activity ratio in sea water samples from oceanic regions by more direct methods. With the exception of the Pacific samples, which had very low activity ratios, the mean activity ratio in Moore's water samples was 0.25.

A somewhat surprising feature of the alpha-pairs data is that over a time scale of one to two years no significant variation in "alpha-pairs" (within statistics) has been observed in the plankton samples. If radium-228 was preferentially accumulated, the pair-rate should increase rapidly in time (see MOORE, 1969b), while if thorium-228 were accumulated preferentially then there should be a significant decrease in activity over a two year period. The fact that no increase or decrease has been observed implies that, in plankton, thorium-228 must be more or less in equilibrium (i.e. within 20-30% of equilibrium conditions) with radium-228.

The data of MOORE (1969a,b) indicates that, on the average, the thorium-228/radium-228 activity ratio in sea

TABLE 15 Thorium isotopes in dry plankton

Sample Number	Th-228 (pc/Kg)	Th-230 (pc/Kg)	Th-232 (pc/Kg)	Ra-226 (pc/Kg)	Activity Ratios		
					Th-228 / Th-232	Th-228 / Th-230	Th-228 / Ra-226
20	44 ± 22	0 ± 4	8 ± 5	760 ± 340	6 ± 3	uncertain	0.06 ± 0.04
21	88 ± 10	6 ± 6	10 ± 7	140*	9 ± 6	14 ± 14	0.63 *
118	22*	3 *	7 *	60*	3.0 ± 1.5	7 ± 7	0.37 *
150	44 ± 24	26 ± 16	28 ± 16	360*	1.6 ± 0.7	1.7 ± 0.7	0.12 *
151	101 ± 24	36 ± 21	36 ± 21	300*	3 ± 2	3 ± 2	0.34 *
164	204 ± 4	16 ± 9	not detected	600 ± 200	uncertain	13 ± 7	0.34 ± 0.11
166	236 ± 54	26 ± 17	29 ± 17	140*	8 ± 5	9 ± 7	1.7 *
181	102 ± 8	14 ± 29	29 ± 29	460 ± 80	4 ± 4	uncertain	0.22 ± 0.04
212	638 ± 216	68 ± 20	34 ± 18	8100 ± 600	19 ± 9	9 ± 2	0.08 ± 0.03
214	1760 ± 220	97 ± 22	26 ± 15	16300 ± 700	68 ± 39	18 ± 2	0.11 ± 0.01
216	860 ± 100	28 ± 24	32 ± 24	3100 ± 1000	27 ± 21	31 ± 27	0.28 ± 0.09
217	788 ± 32	32 ± 22	26 ± 16	3500 ± 1000	30 ± 18	25 ± 17	0.22 ± 0.06
220	562 ± 132	127 ± 42	140 ± 45	1100 ± 200	4 ± 1	4 ± 1	0.51 ± 0.15
232	154 ± 77	not detected	27 ± 19	700*	6 ± 3	uncertain	0.22 *
242	184 ± 8	27 ± 13	11 ± 8	1400 ± 100	17 ± 14	7 ± 3	0.13 ± 0.01

*Error large.

the 15 plankton samples were 34 and 30 pc/Kg dry material respectively. Samples 214 and 220 contained relatively high levels of ionium, and it is interesting to note that the presence of thorium-230 in sample 214 was predicted earlier from the ion chamber (see Fig. 9, Chapter 3). There was unfortunately insufficient sample material to perform an ion chamber run on sample 220.

The large statistical errors in the activity ratios given in Table 15 preclude a detailed discussion, but it does seem that there is a tendency for the throium-228/thorium-232 and thorium-228/thorium-230 ratios to be highest in the Agulhas phytoplankton samples (Nos. 212-217). For all 15 plankton samples the mean thorium-228/thorium-232 activity ratio was 15, a value remarkably similar to the ratio found by MOORE and SACKETT (1964) and SOMAYAJULA and GOLDBERG (1964) for sea water.

Thorium-230 was present in plankton at similar activity levels to thorium-232, the mean thorium-228/thorium-230 activity ratio being about 12. This is in contrast to the sea water data of SOMAYAJULA and GOLDBERG (1966) who found that the activity of thorium-230 was in excess of the thorium-232 activity in sea water by an order of magnitude.

There are evidently many problems relating to thorium in the marine environment still to be solved. At attempt to estimate the biogeochemical balance of thorium is made in Section 5.3.

5.2 Thorium levels from "Alpha-Pairs" Data

The levels of thorium series activity in various marine groups as deduced from the alpha-pairs data are given in Table 16. From published data on the thorium-228/thorium-232 activity ratio in sea water and the similar ratio found in marine plankton, it is reasonable to assume that, in marine life, thorium-228 is the effective (alpha) head member of the thorium series. On the assumption that thorium-228 accounts for one fifth of the thorium series activity, the concentrations of this nuclide have been calculated.

The uncertainty in the thorium-228 content of ocean water (MOORE and SACKETT, 1964; SOMAYAJULA and GOLDBERG 1966, CHERRY et al. 1969) makes an evaluation of the degree by which this nuclide is accumulated by various marine organisms difficult. CHERRY et al.(1969) found that the uptake (accumulation) factor in plankton was at least 2000 if a thorium-228 content of sea water of 10^{-18} g/l was assumed, but pointed out that data from the Walvis Ridge area, where the thorium-228 content of sea water was found to be 27×10^{-16} g/l, indicated an accumulation factor by plankton of only 10.

It has been shown in Section 5.1 that the thorium-228/radium-226 activity ratio in sea water and plankton appear on the average to be similar, viz. about 0.3. If we now consider a radium-226 content of sea water of 4×10^{-14} g/l (BROECKER et al. 1967; SZABO 1967) then the thorium-228

TABLE 16 Mean thorium series activities in various marine organisms (errors are standard errors of the mean)

Organism	No. of Samples	Thorium Series Activity		Th-228 Concentration	Accumulation* Factor
		pc/g (dry)	pc/Kg (wet)	10^{-18} g/g wet organism	
Zooplankton	211	0.52±0.04	35± 3	8± 1	800
Agulhas phytoplankton	10	6.2 ±0.4	290±20	70± 5	7 000
Other phytoplankton	24	1.4 ±0.3	80±15	19± 4	1 900
Pelagic fish (whole)	13	0.4 ±0.1	100±23	24± 6	2 400
Demersal fish (whole)	18	0.2 ±0.1	65±34	16± 8	1 600
Demersal fish (flesh)	7	0.1 ±0.1	35±20	8± 5	400
Demersal fish (liver)	4	0.1 ±0.1	35±14	8± 3	400
Mollusc (soft tissue)	15	0.3 ±0.1	75±20	18± 5	1 800
Mollusc (shell)	15	0.3 ±0.1	240±45	58± 11	5 800
R/Lobster (tail flesh)	9	0.2 ±0.1	60±20	15± 5	1 500
R/Lobster (shell)	9	0.3 ±0.1	150±50	36±12	3 600
R/Lobster (digestive gland)	9	0.2 ±0.1	90±40	22±10	2 200
Seaweed	13	0.4 ±0.1	75±12	18± 3	1 800

* Considering the thorium-228 content of sea water as 10^{-17} g/l.

content of the sea would correspond to about 1.4×10^{-17} g/l. Thus the accumulation factors given in Table 16 have been calculated assuming that the thorium-228 content of sea water is 10^{-17} g/l, rather than the somewhat lower values quoted in the literature. This would seem to be a reasonable assumption as no time variation in the alpha-pairs data was observed in plankton and as both thorium-228 and radium-228 appear to be accumulated to the same degree. The fact that it is an incompletely unsubstantiated assumption should nevertheless be kept in mind.

The thorium series activity of zooplankton and phytoplankton (excluding Agulhas phytoplankton) confirm the levels of about 1 pc/g dry material reported previously by CHERRY (1964) and SHANNON (1969). The thorium series activity of the other marine groups was about 0.3 pc/g dry material. The results, with the exception of mollusc shells, rock-lobster shells and Agulhas phytoplankton, indicate a typical thorium content of about 20×10^{-18}g thorium-228/g wet (fresh) material, with a corresponding uptake factor from sea water to organisms of around 2000.

In zooplankton the thorium series accounted for, on the average, about 5% of the total alpha-activity. The contribution in phytoplankton was typically about 12% and in other organisms it was around 10% although somewhat higher in seaweed (20%) and mollusc shells (40%). There was no apparent increase or decrease in absolute thorium activity along the food chain, and in general the thorium

series elements account for less than 20% of the total natural radiation dose received by marine organisms.

The variations of thorium series activity in the various marine groups are best seen in Fig. 2 (see Section 2.3). In both mollusc and rock-lobster shells, the thorium series elements accounted for an appreciable portion of the gross alpha-activity. If the uranium series activity in the shells is due to radium-226 and daughters, then it would seem that thorium-228 and radium-226 are present in approximately equal activity levels. The data of MOORE (1969b) indicate a mean thorium-228/radium-226 activity ratio close to 0.5 in shells, a value somewhat higher than the corresponding average ratio in sea water. Unless radium-228 is considerably in excess of radium-226 in coastal waters, it is difficult to ascribe the mean thorium-228/radium-226 activity ratio of about unity in mollusc shells to radium-228 decay. It is considered more likely that thorium-228 is present in shells and in marine organisms in general,owing to direct uptake rather than as a decay product. In support of the argument for direct uptake of thorium by marine organisms BHAT et al. (1969) found that thorium-234 which has a 24 day half-life was rapidly removed from the surface layer and concentrated at a depth of 100 m.

The Agulhas phytoplankton were relatively rich in thorium-228 (70×10^{-18} g thorium-228/g wet material). As mentioned previously this plankton was also rich in

radium-226. SZABO (1967) investigated the possible association between calcium, barium and radium, while SOMAYAJULA and GOLDBERG (1966) have drawn attention to the possible association between thorium and barium. It may well be that the phytoplankton species associated with the Agulhas Current accumulate thorium and radium preferentially due to an association with barium. Although there is no direct evidence for this, it is nevertheless a possibility worthy of investigation.

5.3 Biogeochemical Balance of Thorium

SOMAYAJULA and GOLDBERG (1966) estimated the residence times of thorium-232 and thorium-230 in Pacific waters as about 60 to 70 years, viz. times very much shorter than the half-lives of these nuclides. In an attempt to explain the thorium-232/thorium-228 disequilibria and the rapid removal of thorium from sea water, they hypothesised that thorium may be associated with the solid phase.

Let us consider the implications of the measurements of thorium in plankton. Suppose we consider that the concentration of thorium-228 associated with the particulate organic matter is similar to its concentration in plankton (about 2×10^{-16} g thorium-228/g dry material, and that the organic matter content of the upper 100 m layer is 2×10^{-3} g dry material/l- see Section 3.3). Thus the thorium-228 associated with the above would be $2 \times 10^{-16} \times 2 \times 10^{-3} =$

4×10^{-19} g thorium-228/l. Now, data presented in Section 5.2 indicated that radium-228 and thorium-228 are very approximately in equilibrium both in sea water and in plankton, and as explained, extrapolation of fairly reliable radium-226 uptake data indicates that the thorium-228 content of the surface layer of the sea is about 10^{-17} g/l. Thus even in the highly productive surface layer, the thorium-228 associated with particulate organic material would only be a small percentage of the total thorium-228 content of the sea water. The same applies to thorium-232.

In order to calculate the removal times for thorium-228 it is proposed to follow a similar argument to that outlined in Section 3.3 for radium-226. Let us consider that inorganic removal processes are negligible compared with biological removal. Let us further consider that organic matter is removed from the 100 m surface layer at a rate of 6×10^{-2} g(dry)/cm^2/yr (see Section 3.3). If we consider that the thorium-228 content of this matter is 2×10^{-16} g thorium-228/g dry material, then the removal is equivalent to 12×10^{-18} g thorium-228/cm^2/yr and this will equal RN, where R and N have the same meaning as in Section 3.3. Then, taking the thorium-228 content of the upper 100 m as 10^{-17} g/l (i.e. 10^{-16} g/cm^2 = N), the biological removal time for thorium-228 from this surface layer is equal to the reciprocal of R, viz. about 8 years.

A similar argument can be applied to thorium-232. Taking the activity ratio thorium-228/thorium-232 as 15

for both plankton and sea water, the removal time for thorium-232 is also about 8 years. Thus the overall residence times (allowing for radioactive decay as well as biological removal) of both thorium-228 and thorium-232 in the upper 100 m layer must be less than this figure. It should be emphasised that this model is based on several assumptions, and the magnitude of the removal is of an order of magnitude more rapid than that found by SOMAYAJULA and GOLDBERG (1966) for thorium-230 and thorium-232. However, it should be kept in mind that the assumptions about biological removal apply to the highly productive waters around South Africa. In support of the relatively rapid removal of thorium from the surface layer, BHAT et al. (1968) found that thorium-234 was significantly removed biologically in a time scale of about a month. The above removal times should be compared with similar removal times calculated for radium-226 (Section 3.3). Again in the case of the Agulhas Current, the data would indicate more rapid removal.

MOORE (1969a,b) considers that the thorium-228/thorium-232 disequilibria is due to the supply of radium-228 to the ocean by diffusion from thorium-232 bearing sediments. If this were so, then it would be expected that plankton caught in the upwelled waters of the Benguela Current should contain more thorium than plankton found in the vicinity of the Subtropical Convergence. (South Atlantic Central Water which wells up in the Benguela Current is

formed near the surface at the Subtropical Convergence - ORREN, 1966). Data presented in Chapter 6 on the regional distribution of alpha-activity in plankton indicates that the Benguela plankton contained three times as much thorium as its counterpart from the Convergence Region. Thus a possible explanation of the enrichment is that of diffusion from the sediments in the Benguela Current System. On the other hand plankton collected in Sub-tropical Waters had a similar thorium content to that from the Benguela Current, while Agulhas plankton had a significantly higher thorium content.

It is evident that much remains to be done before the hypothesis of MOORE (1969b) can be confirmed with certainty, but there is every reason to suppose that, even allowing for its short half-life, radium-228 may be introduced directly into surface waters from the sediments in coastal regions. The rates of upwelling and vertical mixing in the upwelling areas are much more rapid than rates of vertical diffusion in the deep sea and would explain the apparent anomalies queried by SOMAYAJULA and GOLDBERG (1966). More observations will be required before the problem can be positively resolved.

6. GENERAL

6.1 Variations in Alpha-activity of Plankton

The variations of total alpha-activity, excess polonium-210 and thorium in various marine groups have already been discussed at length. The two hundred odd zooplankton samples however warrant further discussion.

Firstly, let us consider the seasonal variations of alpha-activity in zooplankton. For two years, plankton samples were collected monthly at stations 24-1.5 and 24-5 along the West Coast. (Station 24-1.5 is situated 5 miles off the coast in upwelled water of the Benguela Current, while 24-5 is situated 75 miles from the coast in oceanic water). Although attempts were made to collect both zooplankton and phytoplankton at both stations each month, only the zooplankton records are complete. The phytoplankton could only be collected in sufficient quantities during blooms and the lack of continuous data precludes a discussion of the variations in phytoplankton activity.

The monthly variation of total alpha-activity, unsupported polonium-210 and thorium series activity of zooplankton as well as the surface water temperature and salinity at the two stations are shown in Figs. 19 and 20. In instances where more than one type of zooplankton was collected at a particular station in a particular

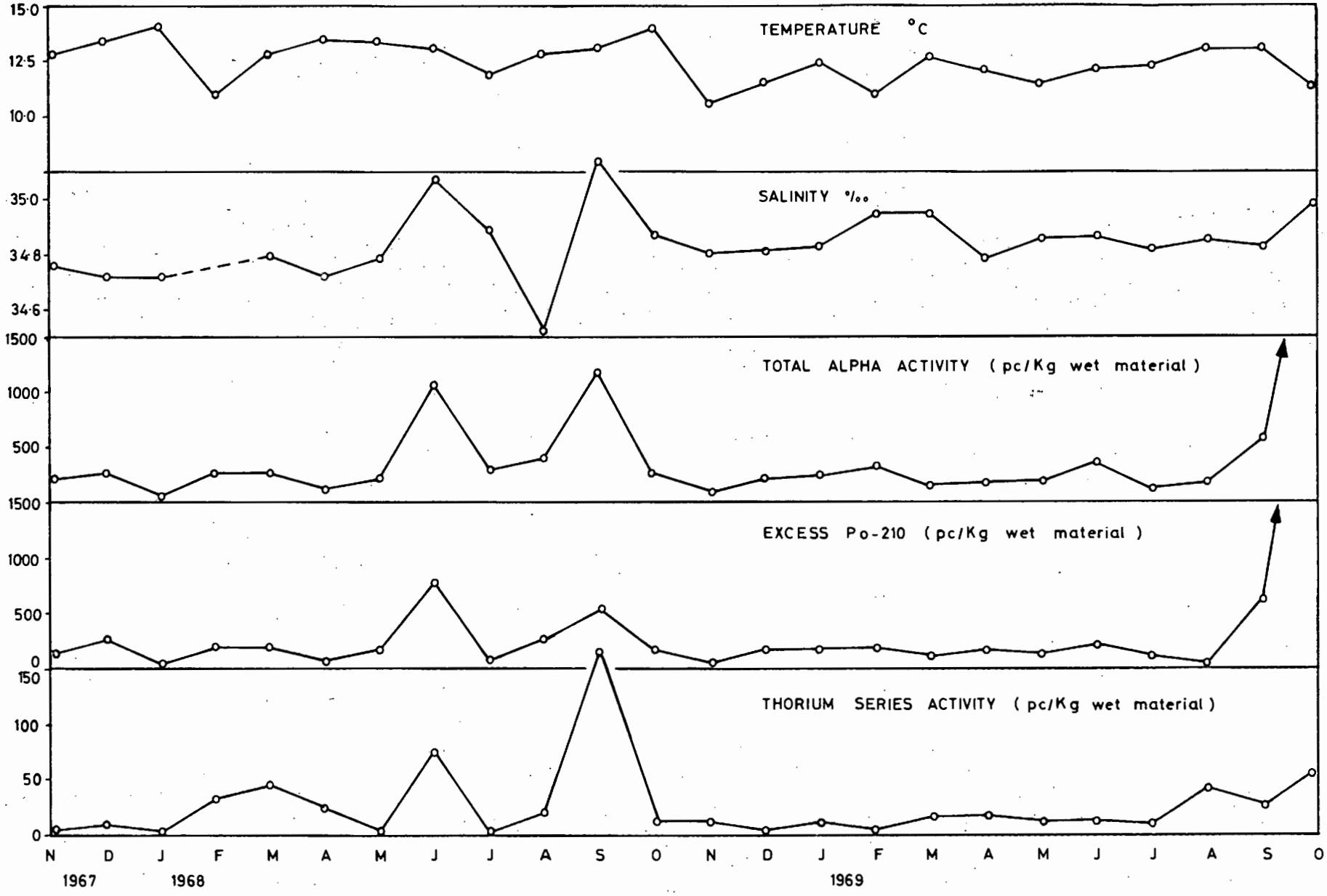

FIG.19 VARIATIONS AT STATION 24-1·5

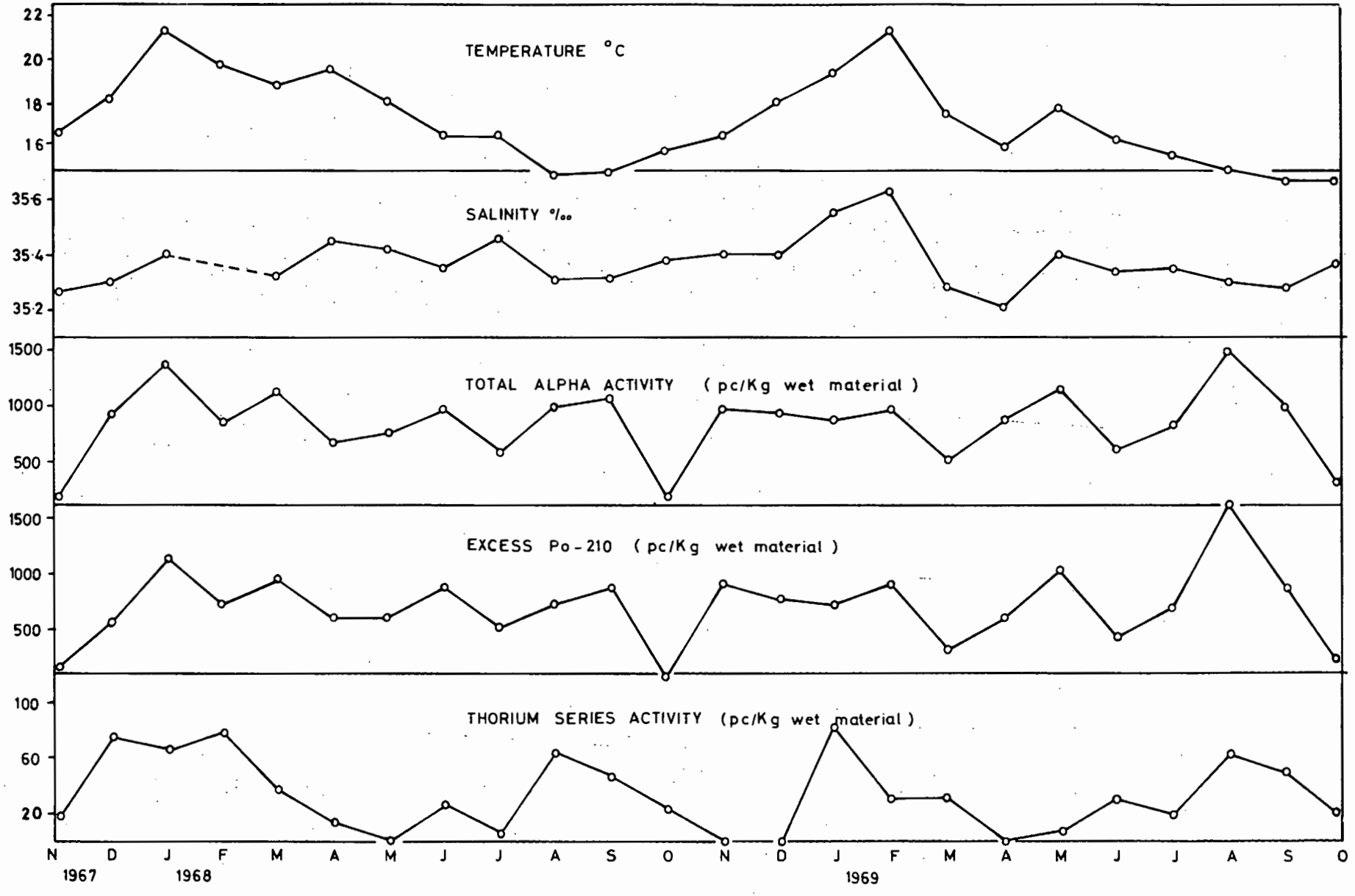

FIG. 20 VARIATIONS AT STATION 24-5

month, the results have been averaged out.

As unsupported polonium-210 accounts for a considerable proportion of the total alpha-activity, it would be expected that these parameters should exhibit similar trends. This is observed in the figures. There is little reason to expect the thorium series activity to display these trends. However, inspection of Fig. 19 (Station 24-1.5) shows quite clearly that there is a marked similarity between the thorium and total-alpha curves, even though the thorium series accounted for only about 10% of the total alpha-activity. In the case of the outer station 24-5, these trends are not so clearly defined.

An interesting feature of Fig. 19 is the apparent dependence of the zooplankton alpha-activity on sea water salinity. During months of high salinity, which correspond to minimum upwelling conditions, high alpha-activities were recorded in zooplankton. During August 1968 when the salinity was low due to the influx of fresh water into the region from the Berg River, which drains much of the Western Cape winter rainfall area, a lower activity was recorded. It does seem as though zooplankton associated with freshly upwelled water has a lower total alpha-activity than plankton associated with minimum upwelling conditions when more typical oceanic water is present. The temperature variation shows little correlation with any of the other parameters at station 24-1.5, and in this connection it is interesting to note that SHANNON (1966) considered that

salanity,being a more conservative property, was a better indicator of upwelling than temperature.

The alpha-activity at station 24-5 showed little correlation with temperature or salinity and the variations in activity appear to be random. One positive feature of the data however is that the alpha-activity was lowest at approximately the same month (October to November) each year, viz. spring conditions.

In order to evaluate the differences between upwelled and oceanic water, the average activities of several copepod species, were calculated, and these are given in Table 17.

As several copepod species are usually present in a given sample, the values given in Table 17 represent average activites of several copepod samples containing the same dominant species. The two species most commonly associated with inshore upwelling and mixing conditions, Centropages brachiatus and Calanoides carinatus exhibited a total alpha-activity typically about one third that of the warm offshore water genus Eucalanus (the latter is often found in the Agulhas Current). Metridia lucens which is almost exclusively found very close inshore in cold upwelled water also contained similar low activities. In particular, Metridia lucens exhibited the lowest level of unsupported polonium-210 of any of the copepod species. However it did contain more uranium series activity than Calanoides carinatus and Centropages brachiatus. The

TABLE 17 Alpha-activity in copepods (fresh/wet)

Errors given are standard errors of the mean

Dominant Species	No. of Samples	Total Alpha Activity	Excess Po-210	Thorium Series	Environment
		pc/Kg(wet)	pc/Kg(wet)	pc/Kg(wet)	
Calanoides carinatus Centropages brachiatus	26	480 ± 75	350 ± 75	25 ± 5	Inshore, upwelling and mixing-cool
Metridia lucens	4	480 ± 160	260 ± 110	50 ± 50	Inshore, cold-upwelling
Eucalanus spp.	12	1280 ± 90	1170 ± 130	85 ± 10	Offshore, warm water
Nannocalanus minor	10	820 ± 140	690 ± 130	35 ± 10	Warm and mixed
Pleuromamma spp.	9	950 ± 110	730 ± 140	45 ± 12	Mixed
Clausocalanus spp.	15	920 ± 160	690 ± 80	30 ± 7	Mixed
Oithona spp.	7	580 ± 170	290 ± 100	65 ± 40	Mixed, tolerant of warm and cold water

copepod species , characteristic of oceanic water and capable of withstanding warm or cold environmental conditions, displayed activities intermediate between those of the upwelled and warm water species.

It would seem that zooplankton associated with warm offshore water are enriched in polonium-210 to a greater degree than species found in the cold upwelled water inshore. This is probably due to variations in the polonium-210 content of the sea water. In support of the findings relating to zooplankton, the mean level of excess polonium-210 in 7 samples of Skeletonema costatum, a species of phytoplankton found only in cold water, was 150 pc/Kg wet material, a value lower than the average for phytoplankton (about 300 pc/Kg).

From the above it is evident that the alpha-activity of plankton must depend to a large extent on species and oceanographic locality. It is proposed to investigate the dependence on the latter more fully.

6.2 Alpha-Activity as an Oceanographic Indicator

The possibility of using natural alpha-emitting nuclides, in particular the isotopes of radium and thorium, for the determination of mixing and circulation patterns in the sea has been noted by several authors.

KOCZY (1958) discussed the vertical distribution of radium-226 in the oceans and suggested that it reflected

radioactive decay during the period in which surface water was isolated from the deep sea. CHOW and GOLDBERG (1960) however suggested that the deficiency at the surface could be generated in the same way as that for silicon and phosphorous, namely association with particulate matter. BROECKER (1963) proposed a four layer ocean model to explain simultaneously both radium-226 and carbon-14 data. More recently BROECKER et al.(1967) presented data on both radium-226 and radon-222 from which the coefficient of eddy diffusion could be calculated. SZABO (1967) however warned that the significant biological removal of radium from the surface layer should be taken into account if the radium-226 distribution is used for tracing ocean circulation.

The somewhat conflicting hypotheses of MOORE and SACKETT (1964) and SOMAYAJULA and GOLDBERG (1966) relating to the thorium-232/thorium-228 disequilibria in the sea have already been discussed. Recently MOORE (1969b) suggested that radium-228 should prove an effective tracer for studying lateral and vertical movements within the ocean applicable to processes on a 3 to 30 year time scale. CHERRY et al. (1969) indicated that thorium-228 may also be useful as an oceanographic indicator.

Let us consider the total alpha-counting data already discussed in Chapters 2, 4 and 5. Table 18 gives the average activities of zooplankton and phytoplankton from six oceanographic regions around South Africa, and these

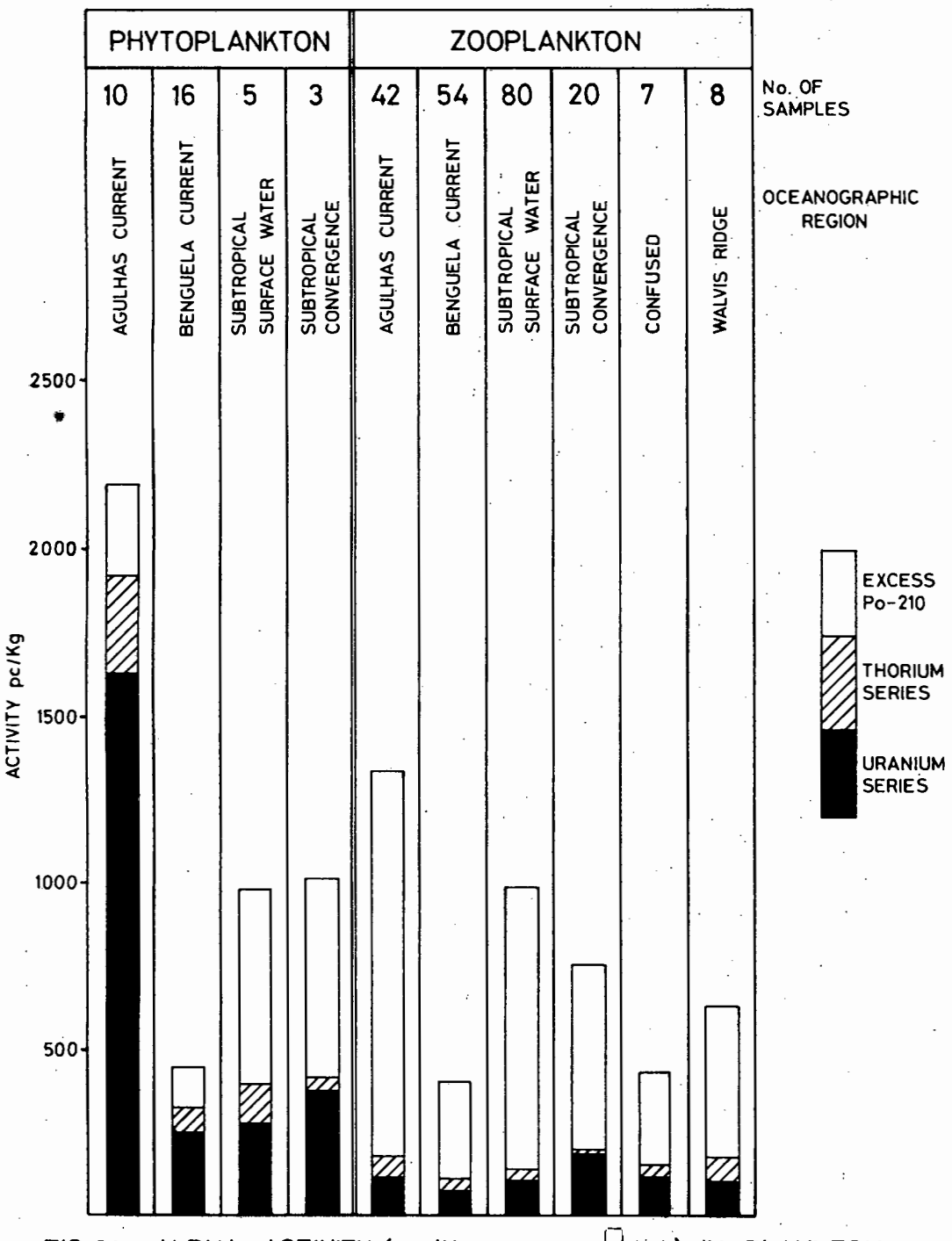

FIG. 21 ALPHA-ACTIVITY (pc/Kg wet material) IN PLANKTON FROM VARIOUS OCEANOGRAPHIC REGIONS

data are shown graphically in Fig. 21. (Note again that "uranium series" activity is the residual activity after deducting the contributions of unsupported polonium-210 and the thorium series from the total alpha-activity).

TABLE 18 Alpha-activity in plankton from various oceanographic loaclities (errors are standard errors of the mean)

Oceanographic Region	No. of Samples	Total Alpha Activity pc/Kg(wet)	Excess Po-210 pc/Kg(wet)	Thorium Series pc/Kg(wet)
		PHYTOPLANKTON		
Agulhas Current	10	2200 ± 400	280 ± 110	290 ± 20
Benguela "	16	450 ± 90	120 ± 40	75 ± 20
Subtropical Surface Water	5	980 ± 130	590 ± 170	120 ± 25
Subtropical Convergence	3	1020 ± 400	600 ± 150	35 ± 15
		ZOOPLANKTON		
Agulhas Current	42	1340 ± 70	1160 ± 100	54 ± 9
Benguela "	54	400 ± 40	295 ± 40	32 ± 5
Subtropical Surface Water	80	990 ± 65	850 ± 70	35 ± 4
Subtropical Convergence	20	750 ± 125	560 ± 100	13 ± 6
Confused area near Tristan	7	430 ± 75	280 ± 65	37 ± 12
Walvis Ridge	8	630 ± 75	460 ± 100	77 ± 11

The high "uranium series" concentration due to radium-226 and daughters in phytoplankton from the Agulhas Current has been discussed at some length in Chapter 3, and it was suggested that this could possibly be ascribed as a characteristic of phytoplankton species associated with this current, or to possible enrichment of radium in Agulhas Water due to upwelling related to the dynamics of the current system. Zooplankton showed little variation in "uranium series" (i.e. essentially radium-226) content. This may be an indication of a fairly uniform distribution of radium in the surface layer of the ocean. However, both zooplankton and phytoplankton collected in the vicinity of the Subtropical Convergence contained typically more uranium series activity (presumably resulting from radium-226) than plankton from Subtropical Regions. Data presented earlier indicate a biological removal time for radium-226 from the surface layer of about 8 years (1 year in the Agulhas Current). The rapid removal of radium-226 would have to be taken into consideration if this nuclide is used as an indicator of circulation. A study of the distribution of radium in the waters around South Africa, especially in the Agulhas Current, may provide a tool for determining not only mixing processes, but also biological activity.

Both zooplankton and phytoplankton caught in the Benguela Current contained less thorium-228 than plankton from Subtropical Surface Water and much less than plankton

associated with the Agulhas Current System, and in view of this it is tempting to postulate the possible association between thorium and radium in the sea. In support of this, both radium-226 and thorium-228 appear to be removed biologically from the surface layer on a similar time scale.

The lowest mean thorium series activity in both zooplankton and phytoplankton was recorded in plankton from the Subtropical Convergence region (see Table 18 and Fig. 21). At first this seemed a little surprising as Central Water, which is formed in the vicinity of the Convergence, later wells up in the Benguela Current. Plankton from the Benguela Current contained on the average three times as much thorium-228 as the plankton from the Convergence region. The fact that Benguela plankton is still lower in thorium than most oceanic plankton may suggest that the enrichment of thorium in Central Water from formation until it wells up in the Benguela Current may be due to the introduction of thorium from the sediments along the West Coast of South Africa. SHANNON (1969) noted that, during 1965, the plankton collected around the Cape contained much less thorium than that collected the following year, and postulated that this may be due to fluctuations in the thorium content of water in Subantarctic regions.

CHERRY et al. (1969) reported that both surface sea water and zooplankton collected in the vicinity of the Walvis Ridge contained above average quantities of

thorium-228. The enrichment of thorium-228 in zooplankton from this region is evident from Fig. 21. ORREN (personal communication) found that copper, iron and manganese were present in surface water in the vicinity of the Walvis Ridge at higher than normal concentrations, although depth profiles indicated that the high values found near the surface were not evident in deeper water.

The Walvis Ridge is obviously a region of considerable oceanographic interest. The coast of South West Africa is a region of strong upwelling and high biological activity, and TUREKIAN and TAUSCH (1964) have reported exceptionally high barium in the tops of sediment cores from the general area near the Walvis Ridge. SOMAYAJULA and GOLDBERG (1966) have drawn attention to the possible association between barium and thorium. Furthermore SHANNON and VAN RIJSWIJCK (1969) have noted an uplift of the lower water masses over the Walvis Ridge. It therefore seems possible that upwelling over the Walvis Ridge introduces thorium-rich suspended matter from sediment tops into the overlying waters. However much additional data for thorium and other trace elements, involving depth profiles and measurements on sediments and particulate matter are necessary before firm conclusions can be drawn.

SHANNON and CHERRY (1967) noted that the concentration of polonium-210 in zooplankton was higher in samples collected offshore than in those collected inshore. They attributed this to the fact that the Central Water which

wells up inshore is away from the sea surface for some time, thus reducing the polonium-210 concentration by both atmospheric sources and radioactive decay. In support of this argument, BEASLEY (1968) observed higher concentrations of lead-210 in amphipods offshore than inshore during periods of active and late upwelling but of low rainfall.

The levels of unsupported polonium-210 in plankton from various oceanographic regions as given in Table 18 confirm the findings of SHANNON and CHERRY (1967), as do the monthly fluctuations in excess polonium-210 over a two year period at a fixed station on the West Coast (Fig. 19). In the inshore region, lowest activities are associated with periods of maximum upwelling - hence the good agreement with salinity data. The level of unsupported polonium-210 in both phytoplankton and zooplankton from the Benguela Current was typically about one third that in plankton caught in Subtropical Surface Water. Agulhas zooplankton on the other hand contained above average levels of unsupported polonium-210. An interesting feature of the data is that zooplankton from the Subtropical Convergence region had a polonium-210 content intermediate between the Benguela samples and those collected in Subtropical Surface Water. Zooplankton from the Walvis Ridge region and the oceanographically confused area near Tristan da Cunha contained lower than average quantities of unsupported polonium-210, and it is considered possible that this may indicate the existance of upwelling in these regions (see Section 10.5).

From the plankton data it seems as though Central Water, which is formed near the Subtropical Convergence and which later wells up along the West Coast is somewhat depleted in polonium-210, presumably due to its isolation from contact with the atmosphere.

In order to ascertain whether the levels of excess polonium-210 in plankton reflected the concentrations of this nuclide in sea water, the horizontal distribution of polonium-210 in sea water at 20 m during March 1969 was plotted in conjunction with salinity data (see Fig. 16, Section 4.1). Attempts were made to correlate the polonium-210 content with currents and water movements around the Cape, and inspection of Fig. 16 of Section 4.1 shows a marked similarity between the polonium-210 and salinity distribution. Arrows have been drawn in to show the movement of a component of the Agulhas Current around the Cape. The salinity of typical Agulhas Water is 35.2 - 35.4^{o}/oo , or about 0.3^{o}/oo lower than South Atlantic Subtropical Water (SHANNON, 1970). Thus the penetration of a tongue of Agulhas Water into the West Coast region about 200 miles offshore as well as an eddy in this intrusion (centred at 35^{o}45'S, 15^{o}32'E) can be seen from both the polonium-210 and salinity data. Typically, polonium-210 values in the intrusion were greater than 25 $\times$ 10^{-15} c/l when the salinity was lower than 35.4^{o}/oo. The eddy had a salinity of 35.29^{o}/oo and a polonium-210 content of 41 $\times$ 10^{-15} c/l. Although data are limited, the polonium-210 distribution

does appear to be closely related to water movements in the offshore region. Closer inshore, upwelling and high biological activity makes the interpretation of the data difficult. The statistical errors of the lead-210 results precluded any accurate comparison with water movements, but it does appear that, on the average, Agulhas Water had a lower lead-210 content than the surrounding water masses.

In summarising, it appears that upwelled water is depleted in polonium-210, and in upwelling regions periods of active upwelling (minimum temperature and salinity) are associated with low levels of polonium-210. However in the case of the Agulhas Current, an inverse relation between polonium-210 and salinity applies. Thus true Agulhas Water (high temperature and a low salinity) contains more polonium-210 than Subtropical Surface Water and upwelled water. The Agulhas Current originates in the high rainfall Equatorial Region where precipitation exceeds evaporation - hence the low salinity. Subtropical Surface Water on the other hand is characteristic of an area where evaporation exceeds precipitation. It is tempting to ascribe the high concentration of polonium-210 in Agulhas Water to increased input by precipitation. Whatever the cause, the distribution of polonium-210 in sea water does agree with the distribution of excess polonium-210 in plankton.

When using trace elements as oceanographic indicators the following view expressed by NICHOLLS et al. (1959) should be remembered - "Certainly the safest generalization

promises to be that for any given chemical element there will eventually be found at least one plankton species capable of spectacularly concentrating it". The degree of biological uptake of polonium-210 by plankton may limit its effectiveness as an oceanographic tracer, but although the removal of polonium-210 from the surface layer is rapid, the rate of input is equally rapid. In view of this, polonium-210 may prove a valuable indicator of oceanographic processes over a time scale of a few months to a year - viz. the time scale of many biological processes in the sea. Its possible use as a measure of biological activity is apparent.

7. CONCLUSION AND SUMMARY

It is felt that the data in this dissertation show clearly that:

(a) Alpha-activity of marine organisms can conveniently be measured by using the sealed sample-phosphor system and total alpha-counting. Activities varied from 200 pc/Kg wet material in the flesh of demersal fish to 15000 pc/Kg wet material in the digestive gland of rock-lobsters, while the typical levels in plankton and pelagic fish ranged from 500 to 1500 pc/Kg wet material. The alpha-activity in marine life accounts for most of the natural radiation dose received by these organisms and places them high on the scale of natural radioactivity.

(b) The alpha-spectrum of plankton is simply measured, without prior chemical concentration, using a large capacity ion-chamber. The information derived from the spectra is largely qualitative, but does show clearly the expected disequilibria involving thorium-228, radium-226 and polonium-210. The ion-chamber data plus total alpha-counting results can be used to obtain useful quantitative information about radium-226 in plankton.

(c) The levels of radium-226 in zooplankton and phytoplankton as deduced from (b) were typically 3×10^{-13} g/g dry material and 1×10^{-12} g/g dry material respectively.

Phytoplankton from the Agulhas Current contained about eight times as much radium-226 as phytoplankton from other regions.

(d) Unsupported polonium-210 accounts for the major proportion of the gross alpha-activity in many marine zoological materials and a lesser fraction in marine plant life. The level of excess polonium-210 is readily measured by repeated total alpha-counting. The results using this method are in good agreement with the chemical extraction and electrodeposition technique for determining lead-210 and polonium-210.

(e) The levels of polonium-210 and lead-210 can conveniently be measured in small sea water samples by solvent extraction followed by alpha-counting and/or alpha-spectrometry. One-and-a-half litres of sea water is adequate for polonium-210 measurements, but is insufficient for rapid and accurate lead-210 determinations. A five litre sample would be more satisfactory.

(f) The levels of polonium-210 and lead-210 in surface sea water around South Africa during March 1969 were about 20×10^{-15} c/l (0.044 d.p.m./l) and 38×10^{-15} c/l (0.084 d.p.m./l) respectively.

(g) Real variations in the lead-210 and polonium-210 content in the mixed layer and in plankton exist and these variations are, in part at least, due to

differing currents and water masses. The possibility of using these isotopes as natural oceanographic tracers is apparent.

(h) Lead-210 and polonium-210 are not in equilibrium in the marine environment, the lead-210/polonium-210 activity ratios in sea water, phytoplankton, zooplankton and pelagic fish being about 2, $\frac{1}{3}$, $\frac{1}{12}$ and $\frac{1}{170}$ respectively. The accumulation factors of polonium-210 and lead-210 from sea water to marine organisms are respectively 4100 and 710 in phytoplankton, 19000 and 815 in zooplankton and 63000 and 200 in pelagic fish.

(i) A correlation exists between the lead-210 and polonium-210 content of zooplankton, the activity of the former being approximately one twelfth that of the latter.

(j) The alpha-activity due to unsupported polonium-210 increases approximately along the food chains (a) sea water - phytoplankton - zooplankton - pelagic fish and (b) plankton - molluscs - rock-lobsters.

(k) Radium-226 and daughters account for most of the long-lived alpha-activity in plankton. Phytoplankton and zooplankton accumulate radium-226 preferentially by factors of about 1100 and 500 respectively. Phytoplankton from the Agulhas Current contained considerably more radium-226 than plankton from other regions.

(l) Thorium series activity can conveniently be measured by the alpha-pairs technique. This activity accounted for 5-20% of the gross alpha-activity in marine organisms.

(m) Thorium-232 and thorium-228 are not in equilibrium in plankton. The thorium-228/thorium-232 activity ratio, as determined by chemical extraction followed by alpha-spectroscopy, is about 15 on the average, i.e. similar to the ratio found in sea water by other workers.

(n) Zooplankton and phytoplankton concentrate thorium-228 from sea water by factors of about 800 and 2000 respectively. The level of thorium-228 in marine organisms was typically 20×10^{-18} g thorium-228/g wet material.

(o) Real variations in the thorium-228 content of plankton occur and these variations show interesting trends from one water mass to another. Highest values of thorium-228 were found in zooplankton and phytoplankton from the Agulhas Current and in zooplankton from the Walvis Ridge region, while low values were recorded in plankton from the Subtropical Convergence and the Benguela Current. The possible utility of thorium-228 as a natural oceanographic tracer is apparent.

In more speculative vein, the data indicate that:

(i) The removal times for lead-210 and polonium-210 from the upper mixed layer are about 5 years

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